

RESEARCHES ON WATER RESISTANT GLUES

BY

S. BUTTERMAN

ARMOUR INSTITUTE OF TECHNOLOGY

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RESEARCHES ON WATER RESISTANT GLUES

A THESIS

PRESENTED BY

SAMUEL BUTTERMAN

TO THE

PRESIDENT AND FACULTY
OF

ARMOUR INSTITUTE OF TECHNOLOGY

FOR THE DEGREE OF

CHEMICAL ENGINEER

MAY 29, 1919

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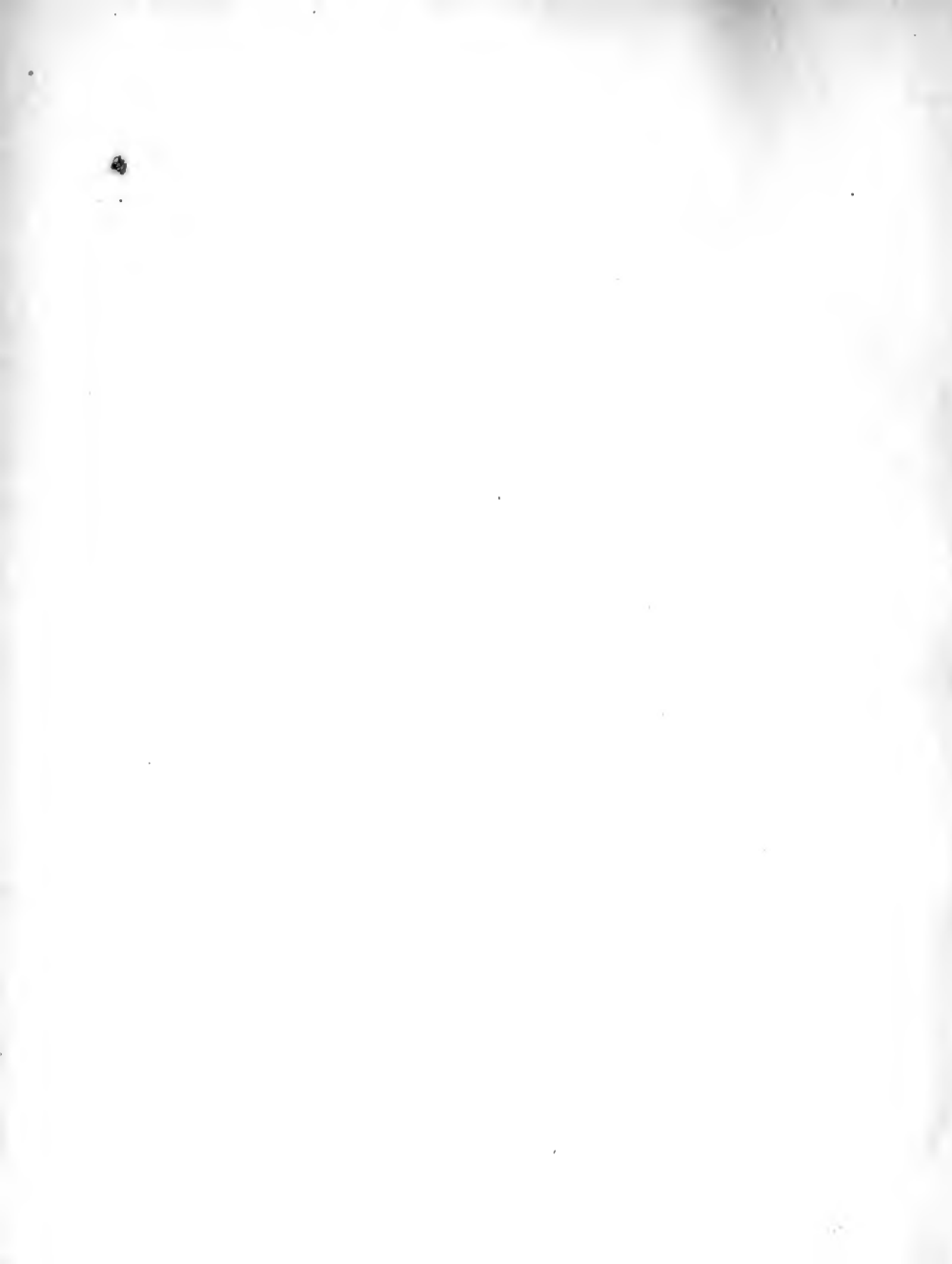


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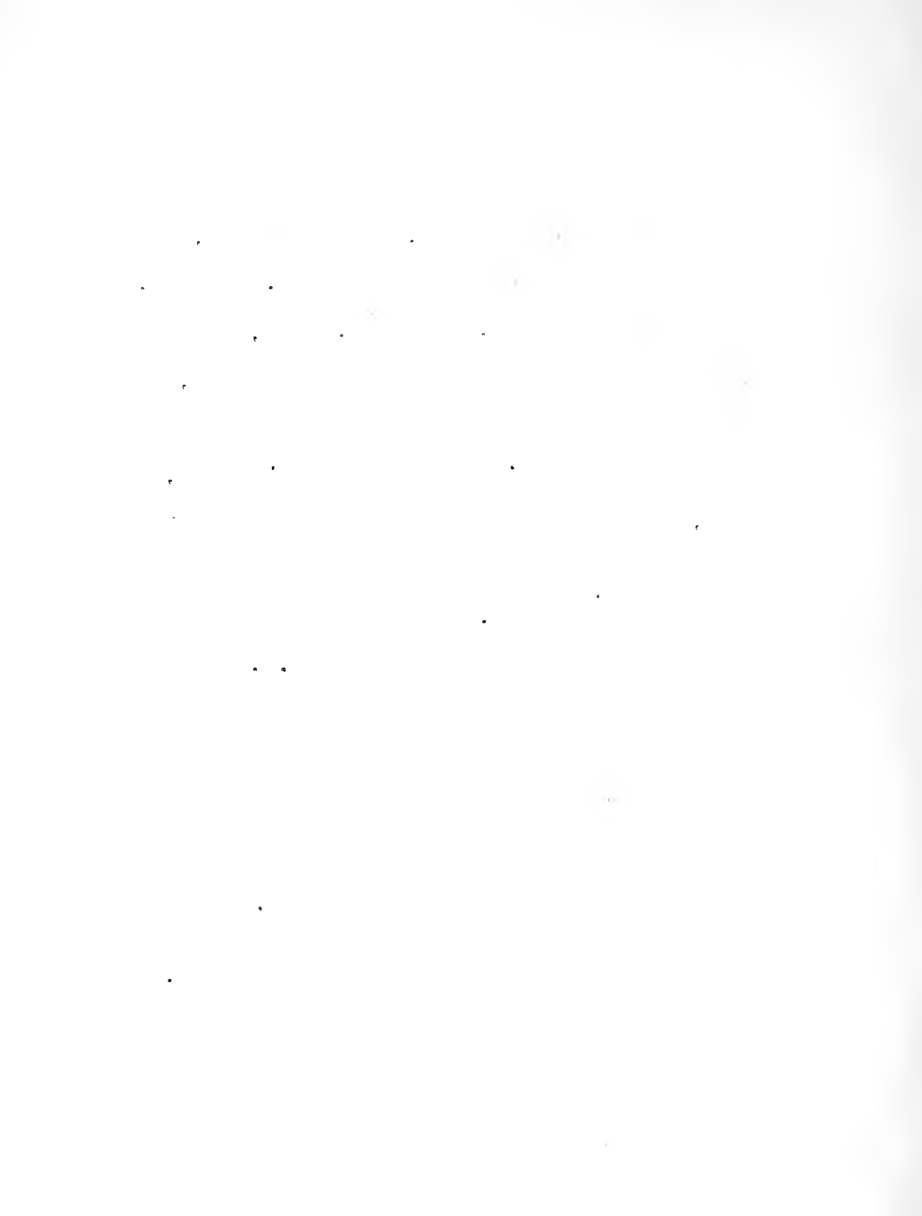
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ACKNOWLEDGMENT

The author desires, at the outset, to express his acknowledgments to Mr. Clyde H. Teesdale and to Mr. George M. Hunt, of the staff of the Forest Products Laboratory, for their valuable suggestions and encouragement rendered during the progress of the work, and, to further express an indebtedness to them for permission to present the following record of research.

S.B.



INTRODUCTION.

Necessity for Water Resistant Glues

Coincident with our entry into the Great War it was rather abruptly realized that an urgent necessity for water-resistant glues for use in aircraft construction existed. In this country relatively little was known at that time regarding the preparation of such a product. During the period of our participation in the Struggle the high price commanded by such a glue stimulated an active competition which has created several satisfactory water-resistant glues that are at present on the market.

The need for glues of this type becomes manifest when it is considered that aircraft parts experience considerable variation in moisture content during the course of flight, by reason of direct contact with clouds, and



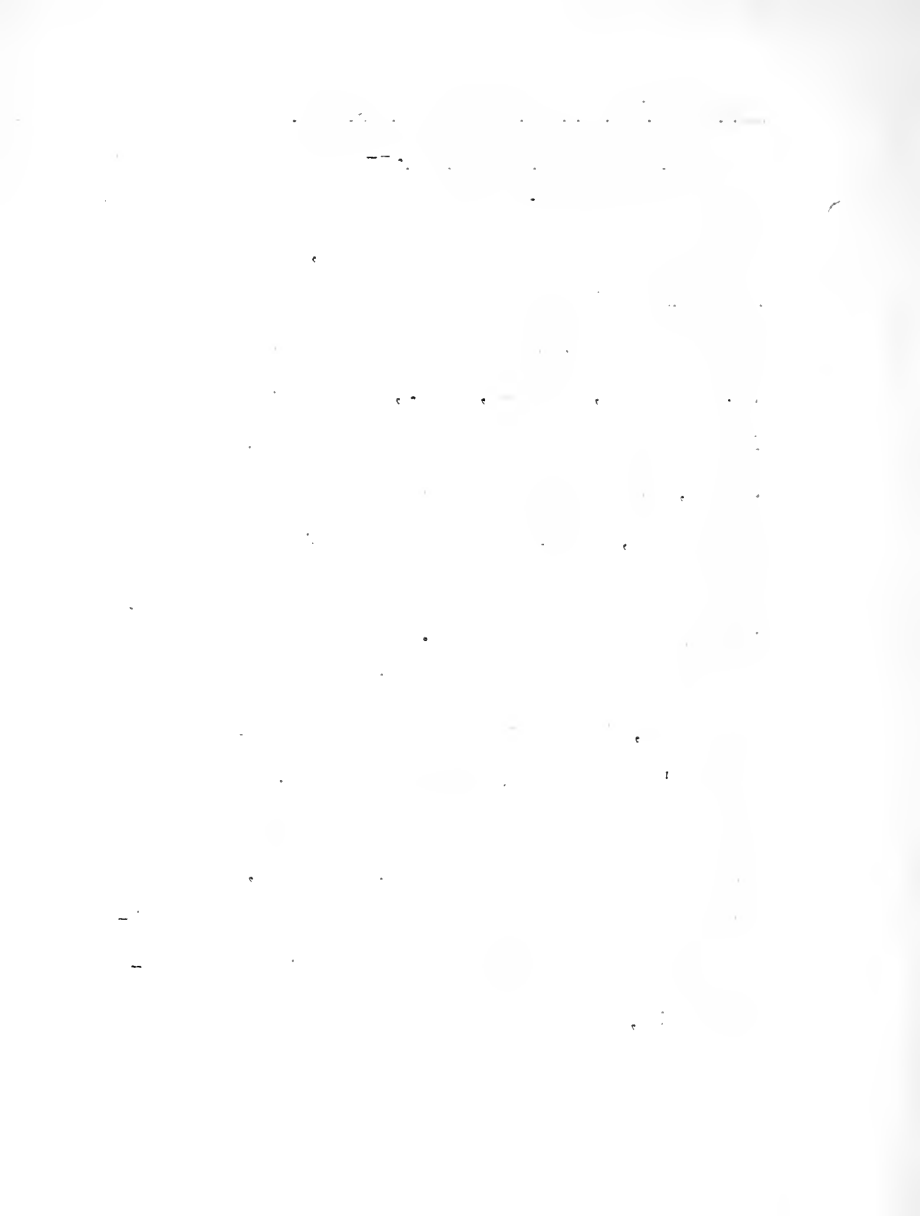
because of the precipitation of moisture upon chilled parts of machines descending from high elevations into the warm air-strata of lower altitudes. Furthermore, before a flight, the air trapped within wing surfaces and confined by wing covering has a relative humidity corresponding to that which exists at the level of the earth; on rising into higher elevations the low temperatures encountered cause saturation of this air to be exceeded and moisture is accordingly deposited upon the wing structures. Again, marked changes in humidity are encountered during storage in the damp holds of vessels transporting planes overseas, and also because of climatic changes. Hence, if danger from loose joints is to be reduced to a minimum, the need for water resistant glues to replace the standard grades of animal glue is obviously urgent in connection with aircraft production.



Application to Aircraft Structures

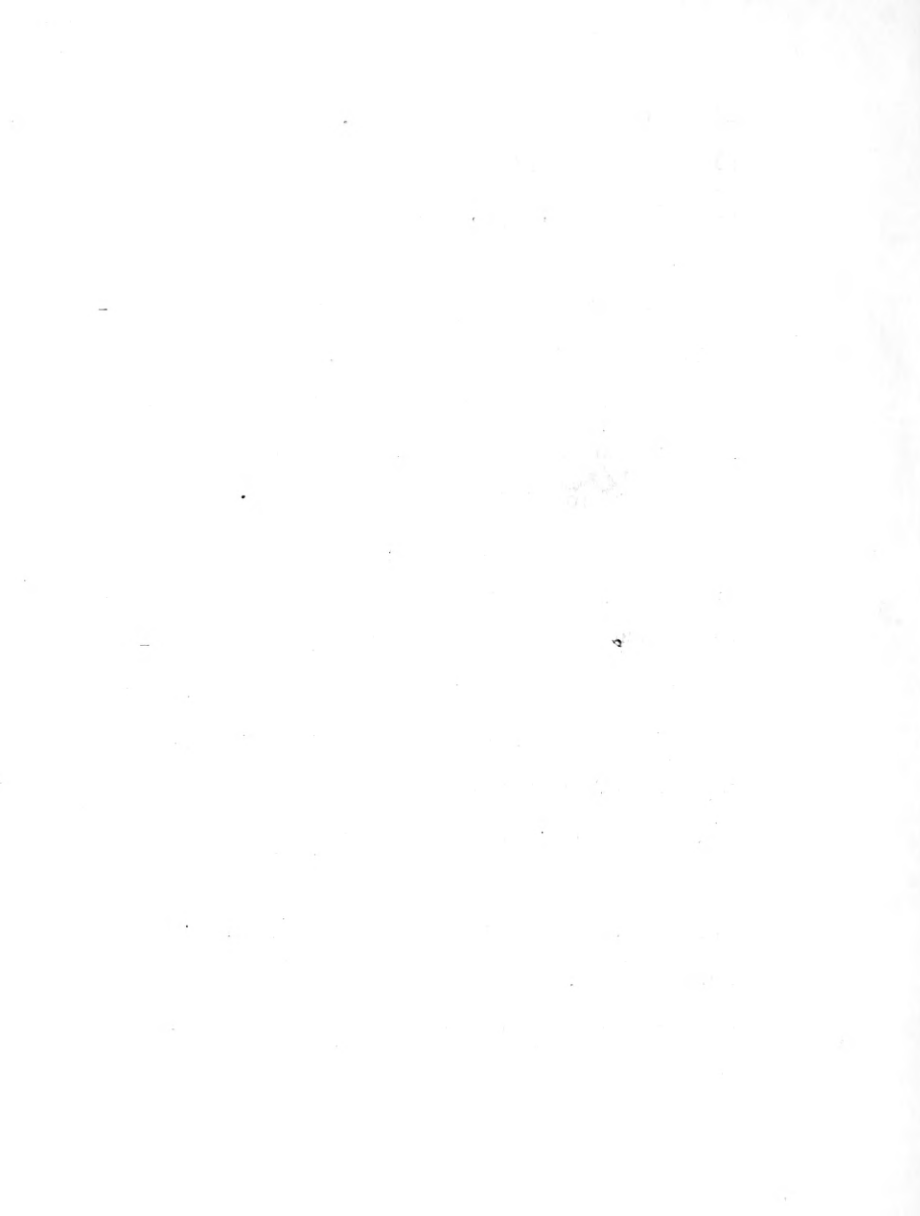
Plywood Construction.--From the fact that every effort is made to decrease the weight of aircraft as far as practical, we find the most predominant structural material employed is wood. In certain elements of construction (wing beams, struts, etc.,) the wood is used in the form of either solid or laminated stock, but where very light structures are necessary, a relatively high development of strength may be obtained only by resorting to plywood construction.

Plywood construction involves the use of a simple, ingenious method of improving upon Nature's method of producing wood. If a thin slab of wood is cut from a tree parallel to the fiber length (not across it), this slab will be found to yield to bending more readily about its vertical axis than its horizontal axis, due to the resistance which the



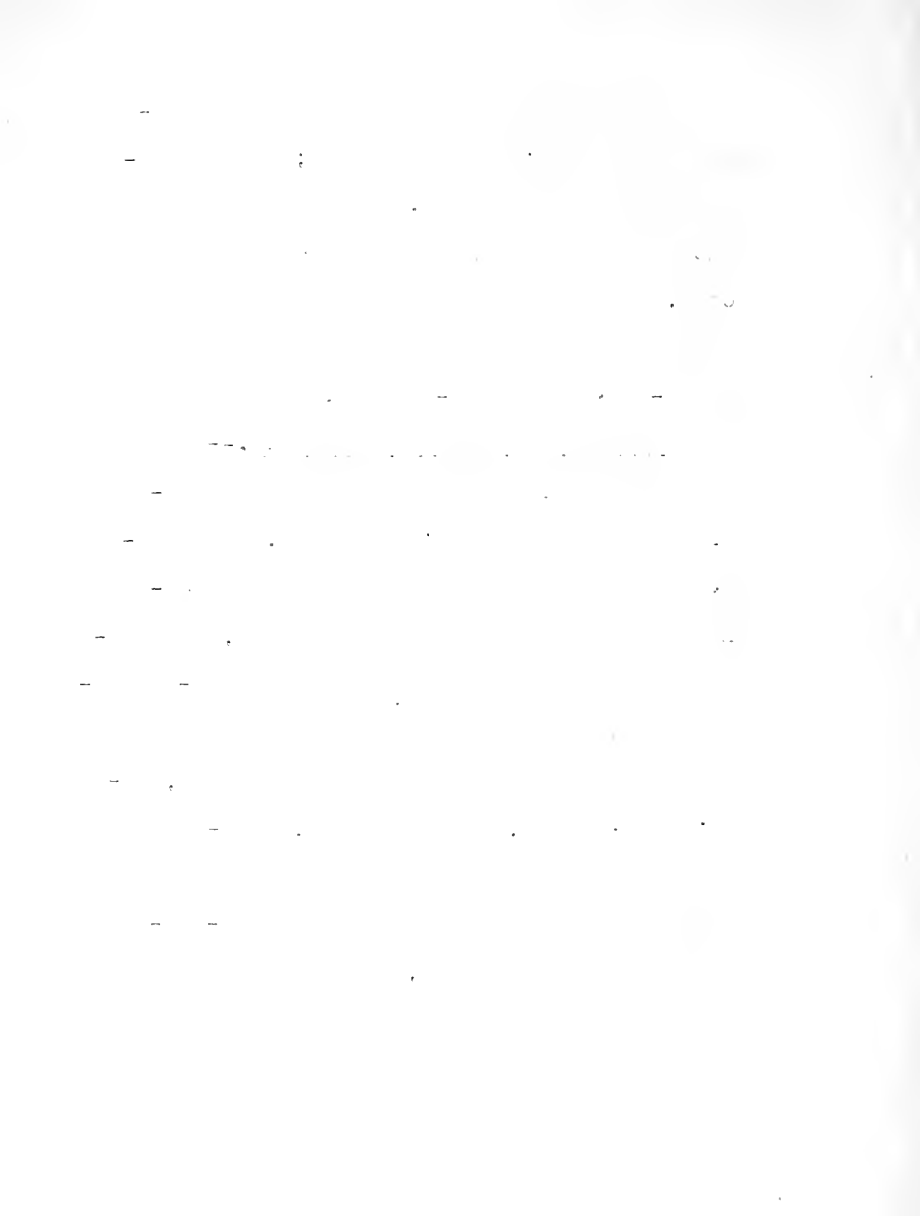
fiber offers to deformation. Hence the thin slab has a negligible amount of stiffness in one direction, and, accordingly for practical purposes has no strength. To overcome this shortcoming the thickness must be increased - which means increased weight.

Plywood construction avoids this difficulty and meets the necessity of lightness by merely combining the thin slab of wood with two others located on either side of it but arranged in such a manner that the direction of grain in the outside plies is perpendicular to that in the central slab. It is this reversal of grain which constitutes the improvement upon Nature inasmuch as the artifice provides resistance to deformation regardless of the direction of the acting force and so creates a member which, for the same weight, is many times stiffer and stronger than solid stock of the same species.



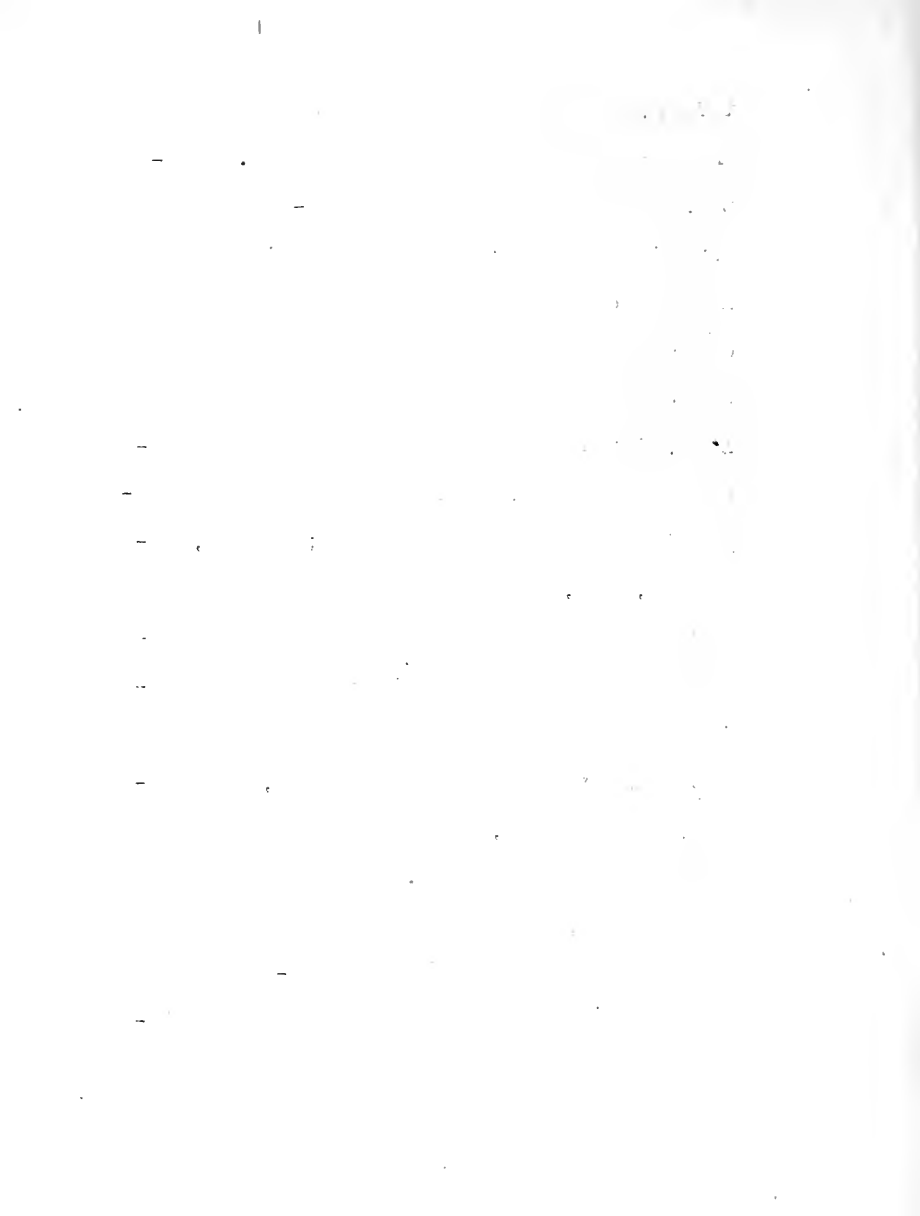
This built up member is called a veneer panel or sometimes plywood; the individual plies are veneers. The outer plies are faces and the central one is designated a core. Where the plywood is built up of more than three plies the central plies are termed cross-bands or cross-banding.

Points of Application of Glue.--The points of application of glue in the airplane are becoming more numerous. The plywood which forms the entire skin of fuselage construction, in most machines, is joined exclusively with some form of water-resistant glue. The use of plywood has also been extended to the manufacture of cowlings, engine bed-plates, aviator seats, wing-rib webs, etc. In the most improved design struts and beams of irregular hollow-section have been devised, in order to reduce the weight of the member per unit of strength;



this necessitates laminated construction and hence involves the use of glue. Furthermore with the aid of water-resistant glue it has become safer to utilize short lengths of stock (heretofore discarded as waste) by resorting to built up structures composed of short lengths combined through lap joints. In the case of propeller manufacture which requires use of the most expensive species of wood (viz; walnut, mahogany, oak, cherry, etc.) production of scrap has been reduced to a minimum by using laminated construction; the rough laminations each differ in shape and length to such an extent as to approximate, when assembled and glued, the peculiar contour of the finished propeller.

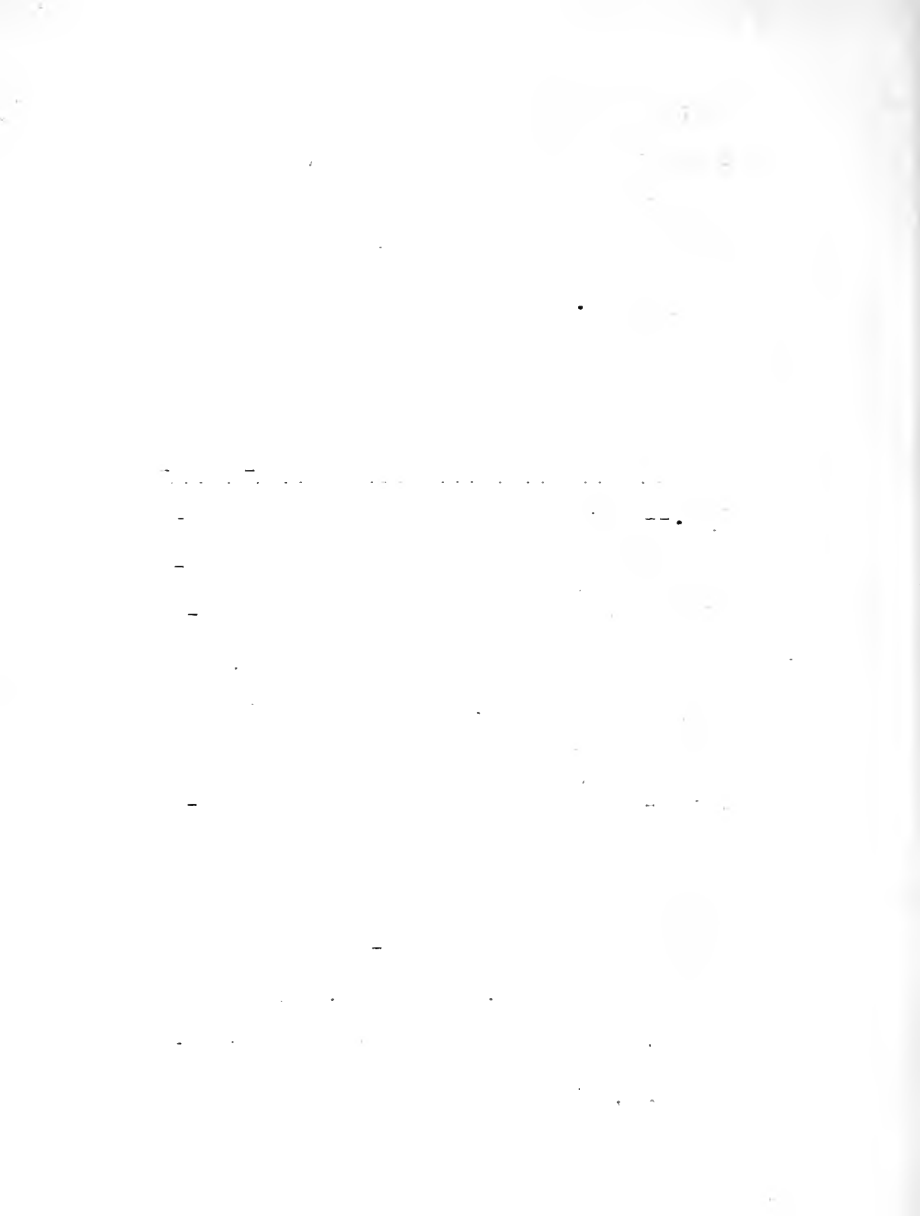
Such practices as these become more practical with the use of water-resistant glues of good quality and are valuable in-



asmuch as they not only reduce initial cost but they effect a conservation of material and so reduce to a minimum the danger of depletion of limited sources of species.

THE PROBLEM

Need for Development of Glue-Formulae.--Early in the period of our participation in the Great War the responsibility for the development of our aircraft program rested with the Signal Corps of the Army. This organization upon becoming aware of the necessity of water-resistant glue for aircraft purposes soon discovered that but one company in the country was manufacturing such a product and this - according to a secret process. Having possession of a secret glue formula by which to manufacture, this company was in a position

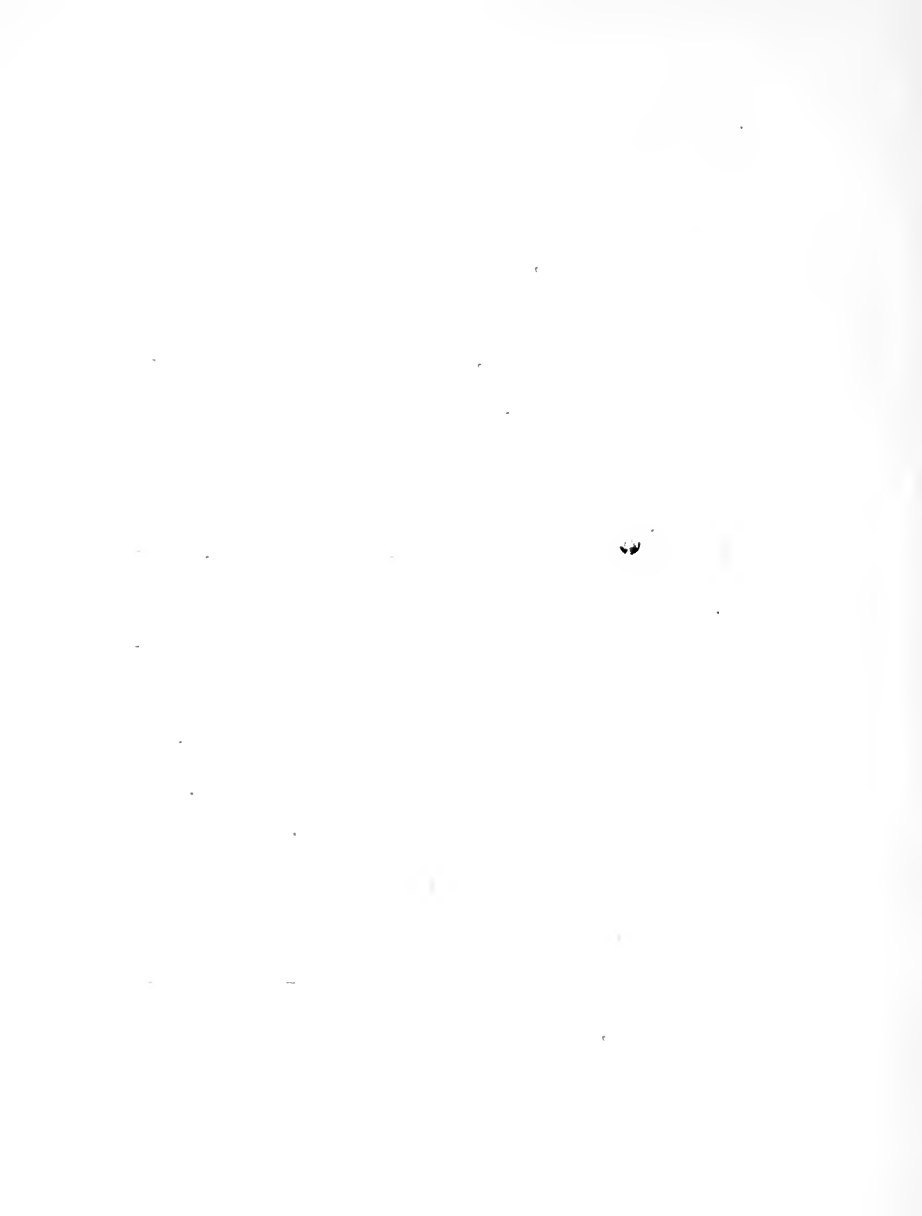


to dictate prices and monopolize the field. Other companies were prevented from contributing to the aircraft program because no glue formulae were available for general use. Since the one company was unable to supply sufficient glue to insure the yearly production of plywood required for the aircraft program, the Signal Corps, in order to insure sufficient production, found itself under the necessity of securing the co-operation of the Division of Forestry, Department of Agriculture which undertook a study to determine methods of preparing water-resistant glues.

It was anticipated that the advantages which would accrue from the development of a high grade glue formula would be several: first, if made

available for general use it would insure an adequate contribution of plywood to the aircraft program; if withheld from general dissemination, mere knowledge of its development should stimulate effort on the part of companies, which had recently entered the field, to improve their product in order to survive competition; thus the tendency would be towards the manufacture of higher grade plywood; furthermore, possession of such a formula would enable the Signal Corps to support stringent specifications (based on the capabilities of the new formula) covering qualities of plywood acceptable for aircraft purposes. Such procedure would likewise serve to promote improvement in grade of commercial plywood.

Statement of the Problem.--The problem then, as encountered by the writer,



was to develop a formula for a water-resistant glue of good quality. The research was to be undertaken at the Forest Products Laboratory at Madison, Wisconsin, in co-operation with the University of Wisconsin.

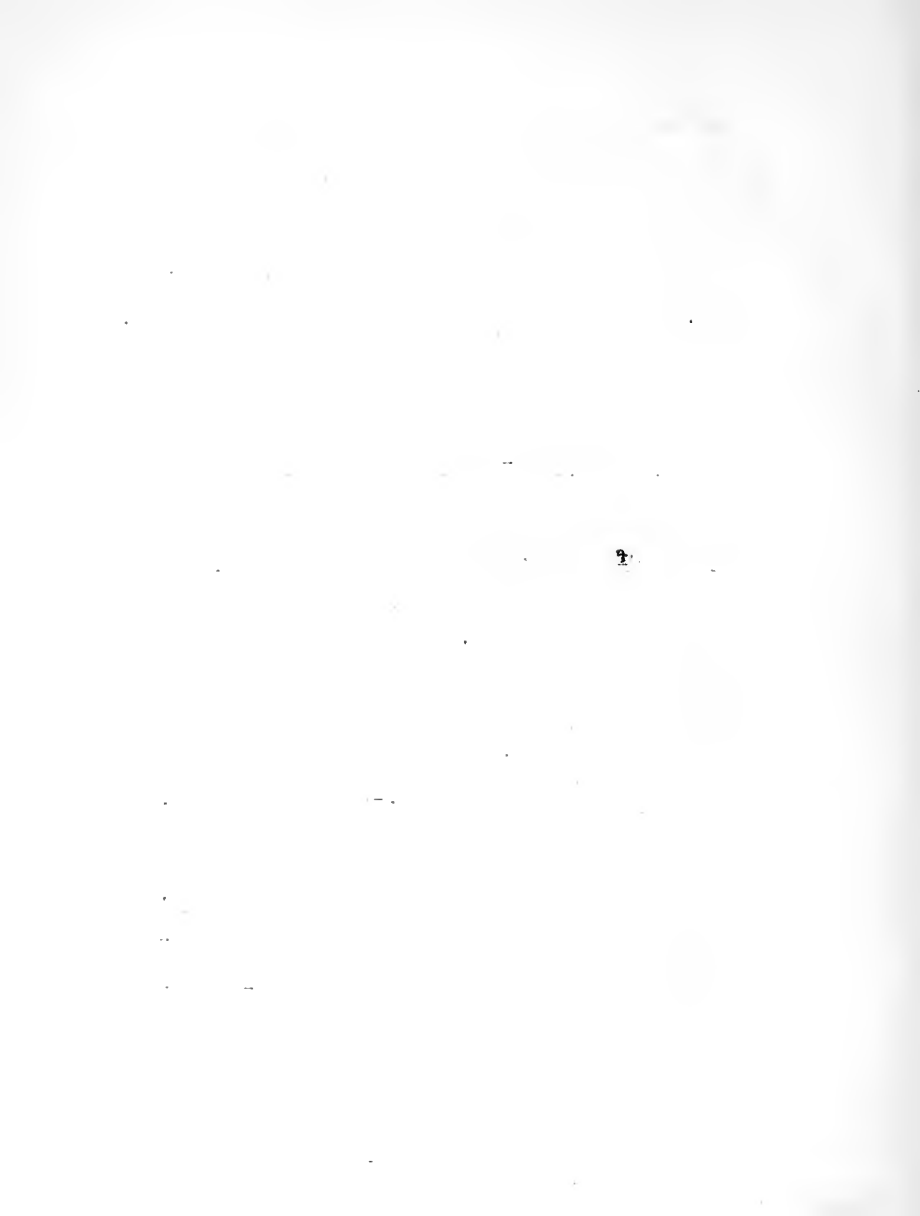
SOLUTION OF THE PROBLEM

Section I - Survey of Available Information

Types of Water-Resistant Glue Available

Two types of water-resistant glue seemed already to be well recognized; one based on soluble blood albumin and the other on casein.

Blood Albumin Glue.--Blood albumin, a product derived from the blood collected in the killing beds of slaughter houses, when dissolved in certain alkaline solutions yields a glue of high water-resistant character upon coagulation of this



solution by heat. This quality is due to the fact that the coagulum formed is insoluble and this behavior constitutes the principle of all glues of the blood albumin type. The disadvantages of this type of glue are that expensive hot plate equipment is required, and special means must be taken to coagulate the glue when heavy stock is glued.

Casein Glue. Closely approaching blood albumin glue in the property of resisting the deteriorating influence of water is the type known as casein glue. Casein itself is the white solid which forms during the familiar souring of milk. The casein, according to available information, could be prepared in the form of glue by dissolving it in milk of lime. A glue so prepared is strictly a "cold" glue and has the extreme advantage that joints made with it

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need not be gotten under pressure quickly, and requires merely the simplest kind of pressing equipment.

Casein - Occurrence, Manufacture, Properties.

Inasmuch as it was desired to develop a glue with casein as a base, it now became necessary to undertake a detailed study of the nature and applications of casein.

Occurrence. Casein occurs as the principal proteid of milk. As a general thing the milk of mammals is an opaque, whitish or faintly yellow liquid (often amphoteric to litmus) consisting of water, fat, casein, albumin, milk sugar (lactose) and inorganic constituents; the most important constituents are the fat and the casein. Cow's milk is the chief variety and shows the following average analysis:

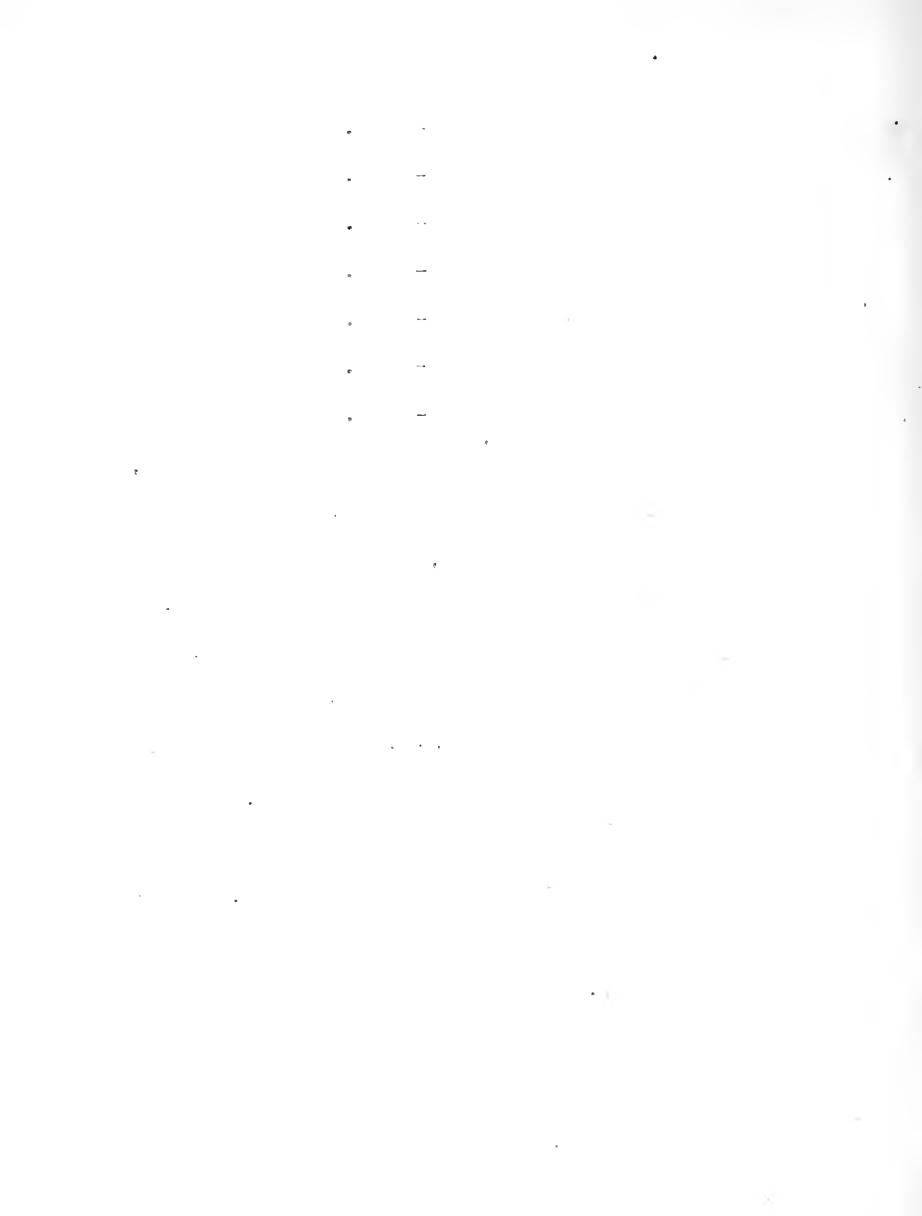


Fig. 1. The relationship between the number of species (S) and the number of individuals (N) for different taxa. (a) All taxa, (b) Insects, (c) Plants, and (d) Fungi.

Fat	-	3.4 %
Casein	-	3.2 "
Albumin	-	0.6 "
Lacto-protein	-	0.1 "
Lactose	-	4.5 "
Ash	-	0.7 "
Water	-	87.5 "

Free casein is not dissolved in milk, but occurs associated with calcium in the form of a suspensoid, as can be proved by filtering milk through a porous earthenware plate; the filtrate obtained consists merely of a solution of milk sugar and saline constituents; the fat and combined casein remain on the filter. The combined casein can also be thrown out unchanged by high centrifugal action, demonstrating again the suspensoid state of its existence.

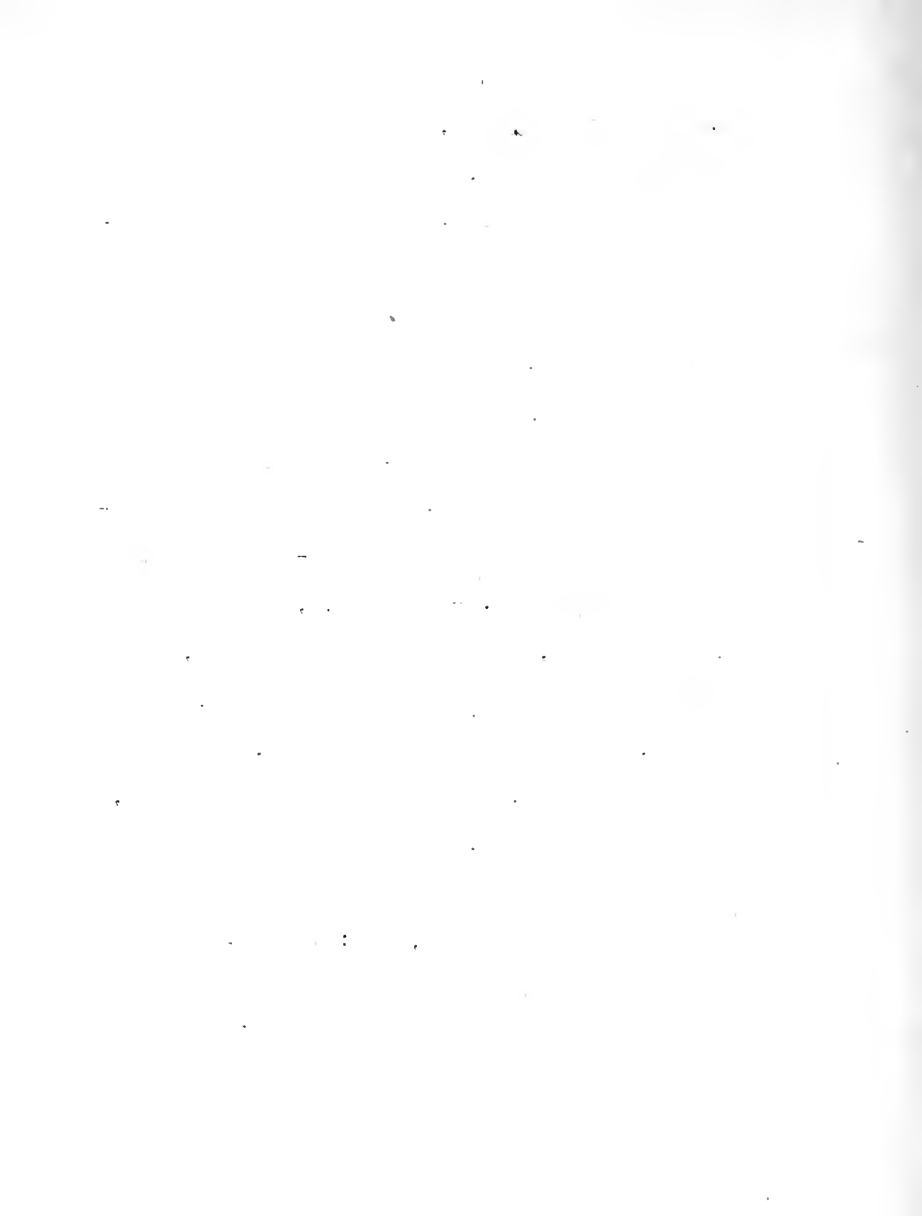
The exact nature of this union of



casein with calcium, in the form in which it occurs in milk, has been the subject of much controversy. Some authorities maintain that the two ingredients are present in stoichiometrical proportions and exist as a true compound; others hold that the calcium is adsorbed by the casein and the union is an adsorption compound. The truth is still a matter of question. The compound is generally designated as calcium - caseinate.

Manufacture.--When fresh, whole milk is left at rest, or is set in very rapid, rotary motion by means of a centrifuge, the cream, or portion richest in fat, collects on the surface, and if this be skimmed off, skim milk remains. This latter is the raw material for the preparation of the second chief product of milk, viz: casein.

Casein is obtained from skim milk by liberating it from its combination with calcium



and taking advantage of the insolubility of the product which is base-free casein or simply - casein. This liberation is effected in one of two ways, viz:

I. Displacement of the calcium by acid using,

Lactic acid

Hydrochloric acid

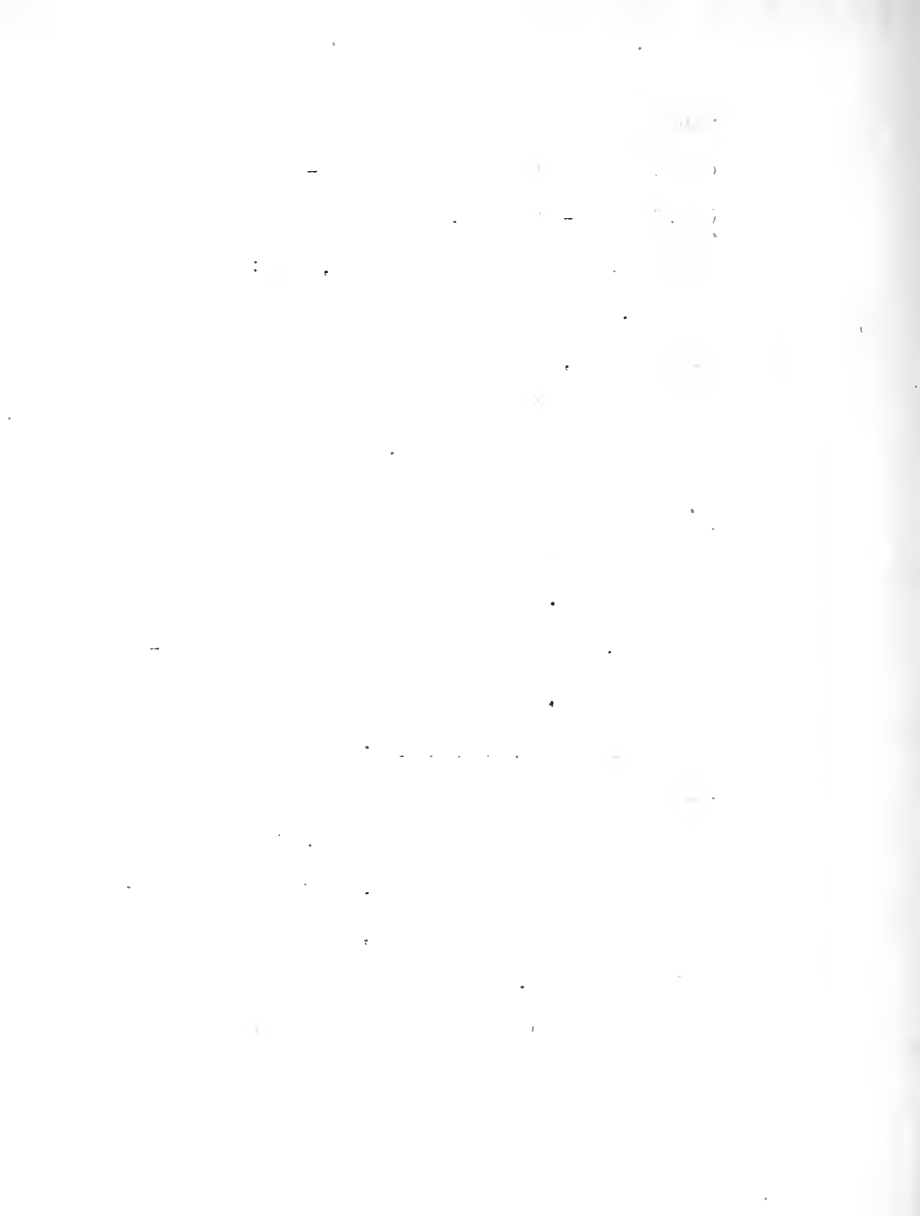
Sulphuric acid

Acetic acid

etc.

II. Coagulation by the chemical ferment rennet.

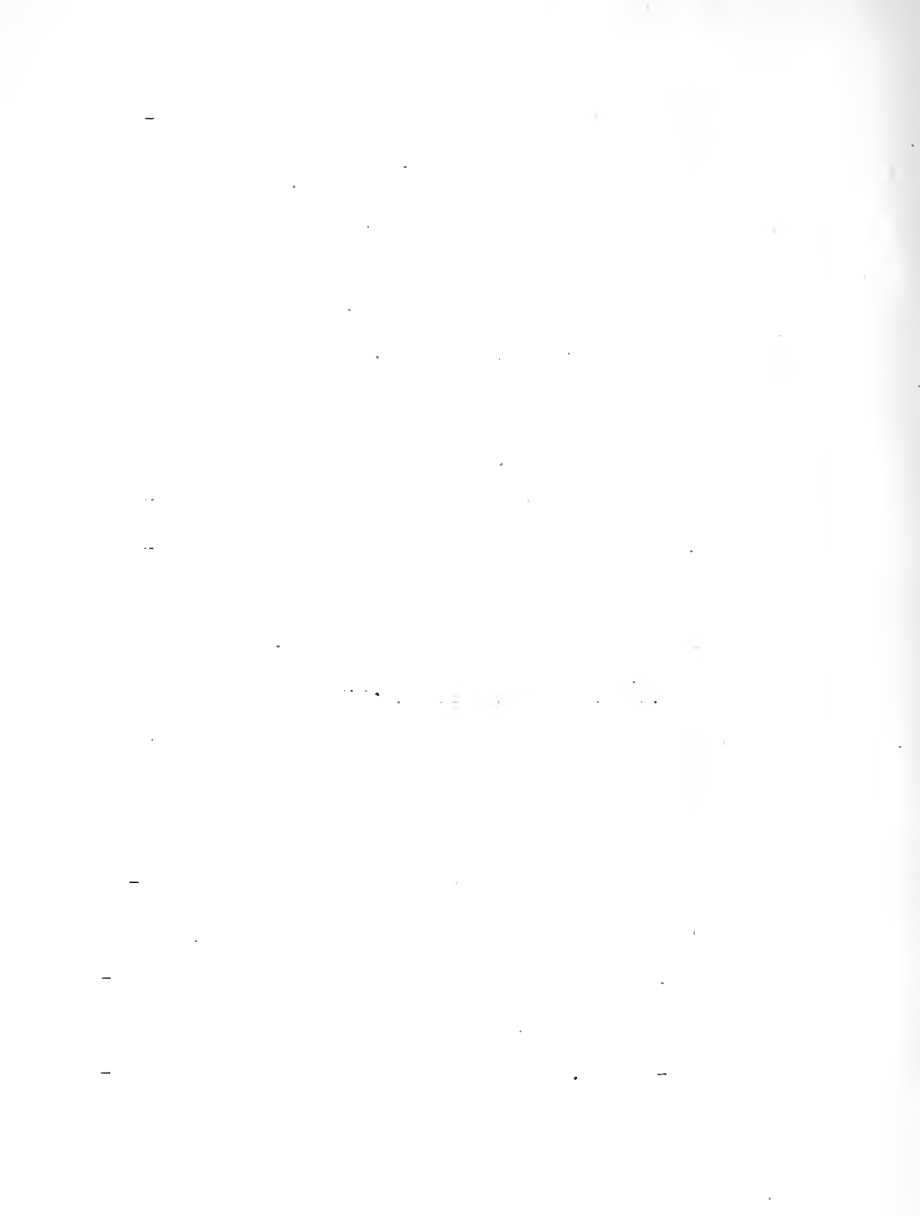
Natural Sour Method. This method of liberating free casein from the combined form in which it exists in milk depends upon the fact that milk, even when freshly obtained from the cow, contains lactic acid bacteria. These bacteria feed upon the sugar (lactose) of milk and one of the



products of their life phenomena (fermentation) is lactic acid. The concentration of lactic acid increases progressively and after some time has become high enough to liberate all of the casein. This is the familiar souring of milk.

The exact nature of the mechanism by which the acid causes the calcium to split off from its combination with casein, whether by simple chemical double decomposition or through adsorption phenomena remains a matter of controversy.

Mineral Acid Method.--The natural sour method of liberating casein requires considerable time because the development of acid is so gradual that a number of hours must elapse before a sufficient concentration is reached to complete the precipitation. For example it is not uncommon creamery practice to allow the process to go on over-night. Commercially the time is mater-



ially shortened by introducing, as a substitute for lactic acid, some mineral acid which is commercially available, such as hydrochloric or sulphuric acids. The acid is introduced in sufficient quantity to raise the concentration to the desired point practically at once. Hence the entire process can be accomplished in about one hour.

Various other acids such as acetic acid, etc., are sometimes used.

Rennet Coagulation.--Rennet casein is obtained by treating skim milk with rennet, a chemical ferment obtained from the fourth stomach of a suckling calf. The rennet process differs from the acid methods in that chemical precipitation does not occur; the action is one of simple coagulation; the solution becomes neither acid nor alkaline.

The result of the action of rennet in

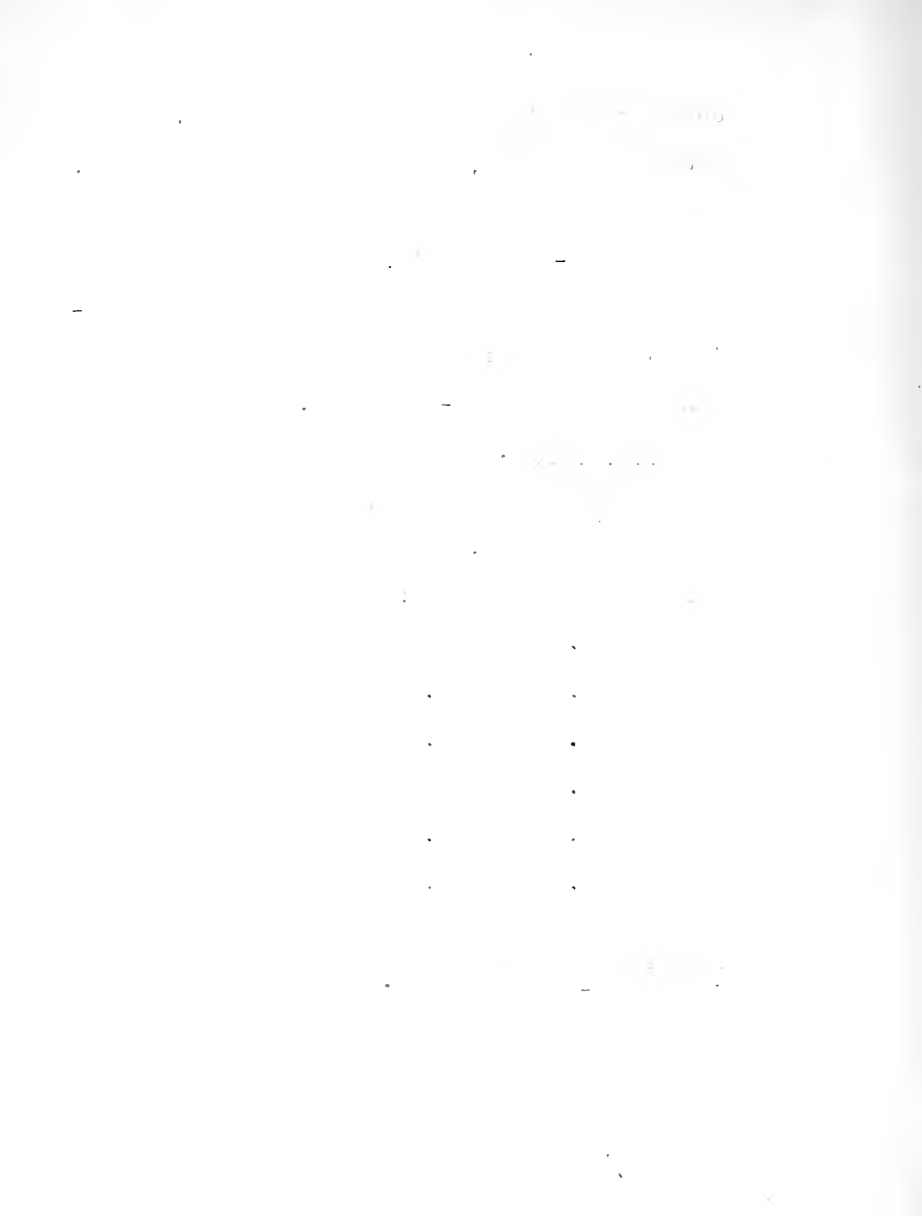
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coagulating milk is wholly unlike the effect produced by acids, from a chemical view point. The curd formed by this action is not the simple base-free casein, but the original calcium caseinate itself with a certain striking modification; this product is generally called calcium para-caseinate.

Properties. Casein is a very complex chemical compound belonging to the general class of proteins. It has the following percentage composition:¹

C	52.96 %
H	7.04 " to 7.53 %
N	15.6 " to 15.91 "
O	22.78 "
S	0.75 " to 0.82 "
P	0.8 " to 0.84 "

¹ Thorpe - Dictionary of Applied Chemistry



From its intimate union with calcium in milk, we find commercial caseins associated with varying quantities of calcium, generally recorded as ash content. The ash content of acid-prepared caseins is given as ranging from 1 to 3 per cent; rennet casein is notoriously higher in ash content ranging from 7 to 8 per cent.

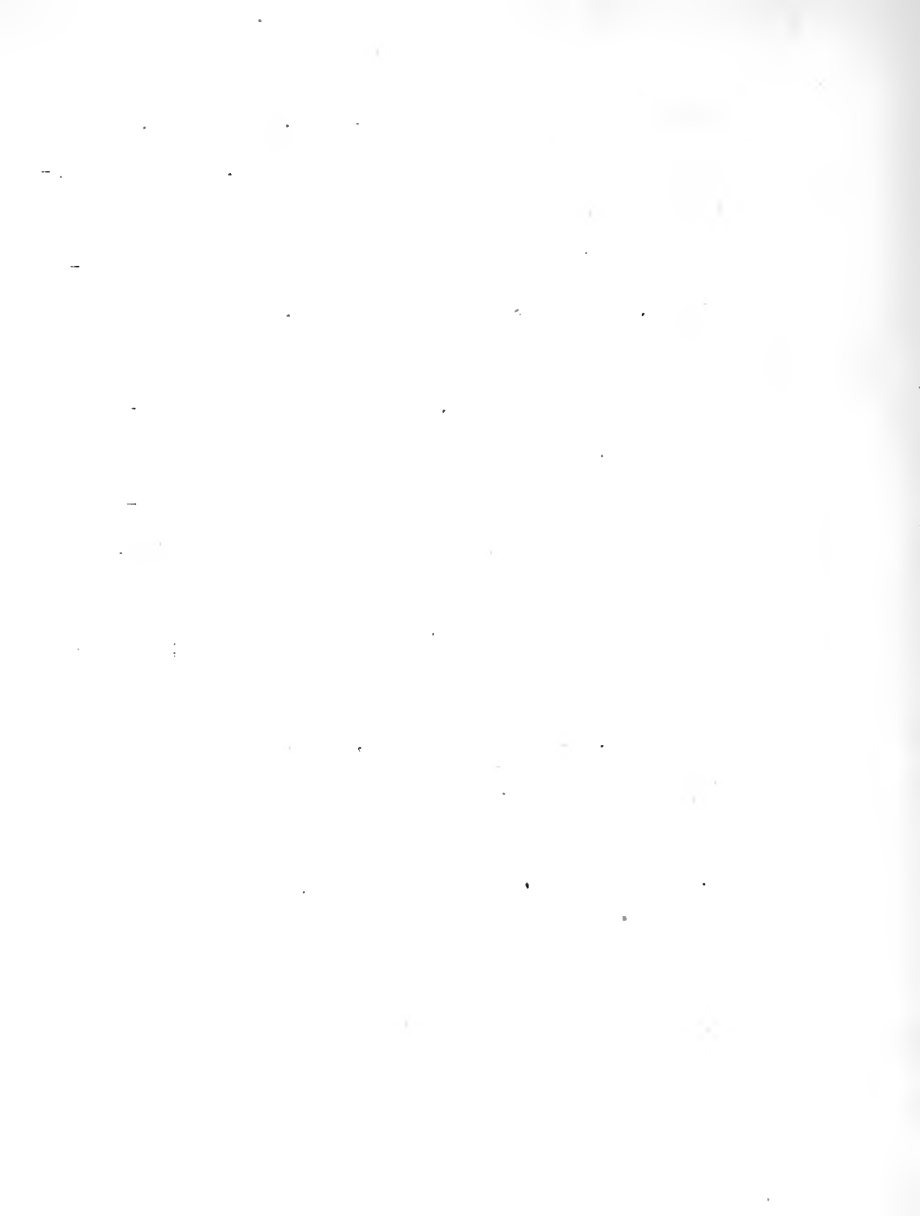
Casein, when pure, is a white amorphous body insoluble in distilled water or very dilute salt solutions. It is soluble in 5 per cent salt solution and in hot 50 per cent alcohol. It is odorless and forms when dry a crumbling, horny mass. It is an amphoteric substance exhibiting the typical dual combining capacities characteristic of proteins.

The basic properties of casein have not been so extensively studied. It dis-



solves easily in moderately dilute acids, more easily at higher temperatures, forming soluble compounds which are either combinations of acid with the protein or decomposition products, depending on conditions. Some hold that simple addition products of the casein and acid are formed, such as casein hydrochloride. These casein salts are very unstable and decompose on dialysis with separation of free casein; they are precipitated from solution by addition of just enough alkali to neutralize the combined acid; treatment with such salts as sodium or calcium chloride, sodium sulphate, etc. accomplish the same effect.

If a "weak" acid such as acetic acid be employed for precipitation, the acidity of the mixture is insufficient (because of limited dissociation) to transform the casein into a base and a considerable excess



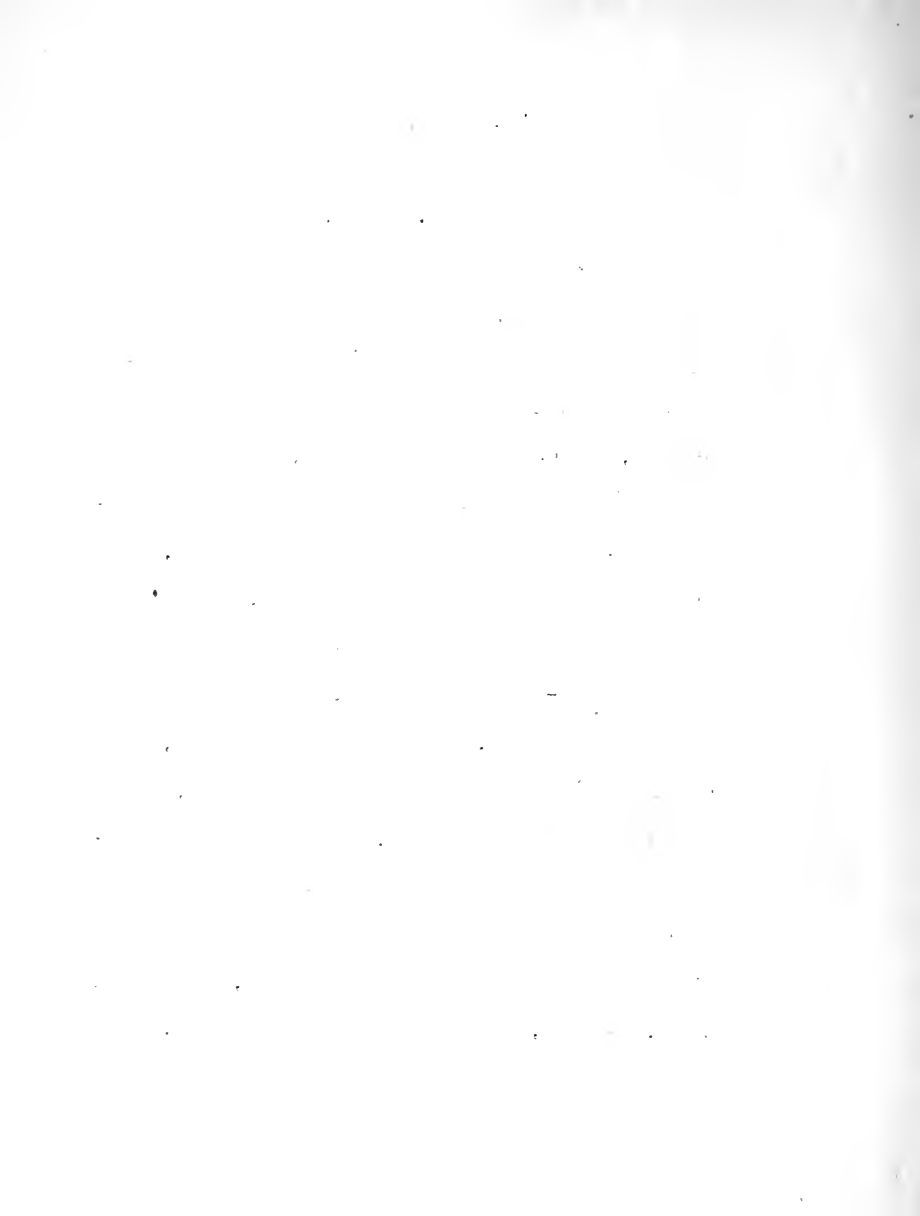
of acetic acid may be added without danger of loss of material through re-solution of the protein. Accordingly for quantitative estimation of casein the precipitant unvariably used is acetic acid. Concentrated acids char ("burn") casein and readily dissolve it.

The acid properties of casein have been more extensively investigated. Free casein suspended in water acts as an acid expelling carbon dioxide from carbonates and bi-carbonates forming a so called salt with the base; and in this way, according to Osborne, the ammonium, potassium, sodium, lithium, magnesium, strontium and calcium caseinates are prepared.

In the presence of alkalies casein likewise exhibits its acid character, uniting with fixed alkalies, ammonia, alkaline carbonates and phosphates, borax,

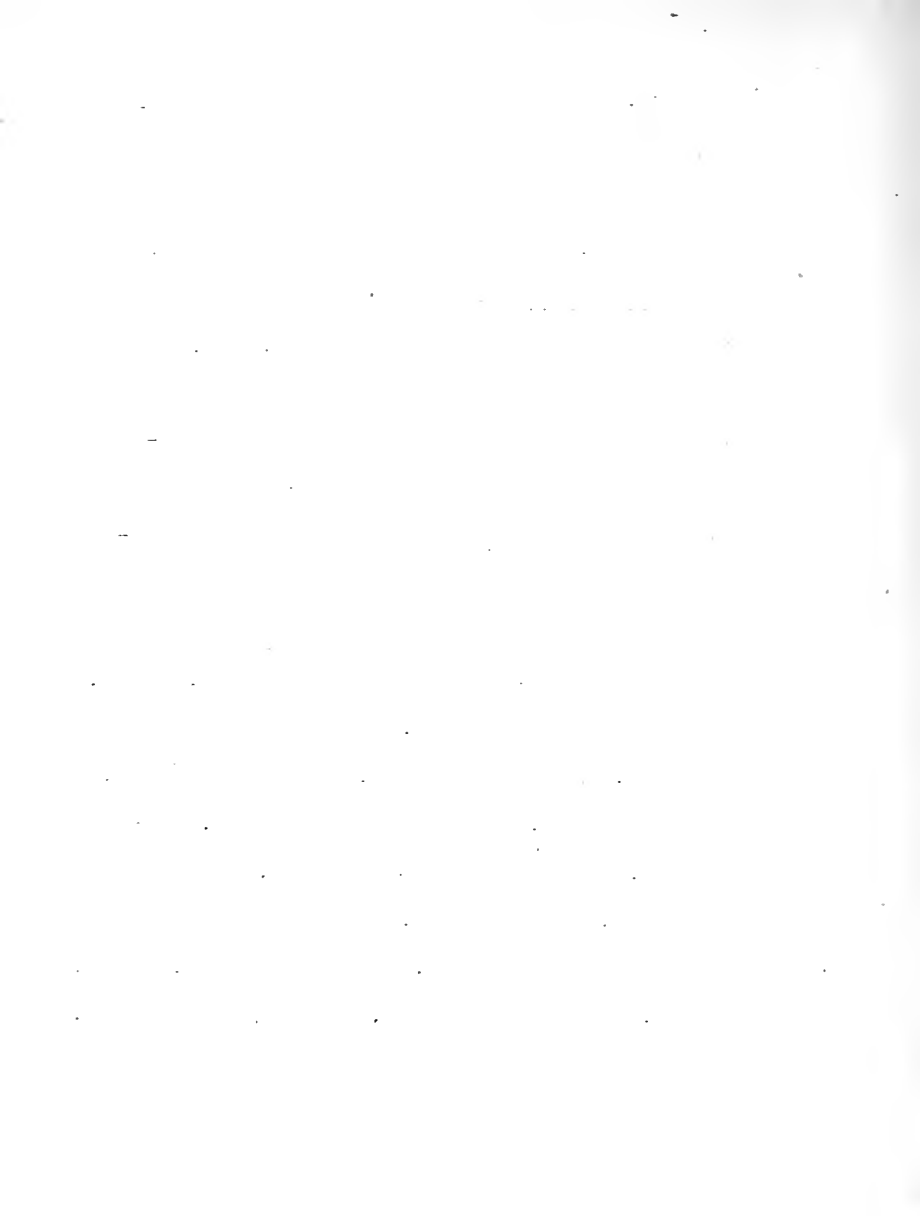
sodium silicate, etc., passing into various states of solution; those with alkalis are nearly transparent and exhibit the least viscosity; the compounds with the alkaline earths give solutions which are opalescent or milky in appearance and of high viscosity. On heating with alkali decomposition occurs, ammonia being evolved; as the hydrolysis progresses the liquid becomes extremely thin. The alkali "salts" of casein, but not those of the alkaline earths, diffuse through porous earthenware.

The so-called caseinates formed above are precipitated, from their solutions, very easily by the addition of dilute acid, (example curdling of milk), the precipitate redissolving in excess of acid. They are also thrown out of solution by sodium chloride and sulphates or magnesium sodium, ammonium, zinc, copper, aluminum and other salts.



Rennet casein or para-casein is identical in properties with free casein with the single exception that it is insoluble in the presence of soluble calcium salts.

Applications. For many years the sole use of casein was as a foodstuff, and, it is only through the scientific researches of the past few decades into the albuminoid substances that attempts have been made to utilize this body technically. At present casein finds an extremely wide range of applications and its uses are becoming more manifold daily. It is used in pastes, glues, card-board manufacture, paper sizing and glazing, leather dressing, soap manufacture, cotton sizing, dressing for textiles, finishing, waterproofing of fabrics, calico printing, cask glazing, artificial bone and ivory, billiard balls, tortoise shells, amber, ebony, picture mouldings, sealing for bottles,



cabinet and pianoforte, making emulsions, fining wines, boot polishes, polishes, films, etc. Furthermore, its original application as a foodstuff has not been lost sight of; its high nutritive value to man and its ready assimilability have led to the preparation of number of artificial foods, viz: Sanotogen, Nutrose, etc.

Casein as a Glue Base.-The employment of casein as a glue base is of fairly ancient date; its property of dissolving in alkaline liquids to form a good mucilage was known to the ancients. Yet it is only in the last thirty years that it has been placed on the markets of Europe under the name "cold" glue. It has not yet made much progress notwithstanding the advantage that such a glue is inodorous, ready for immediate use and requires no heating.

The literature on the subject of casein

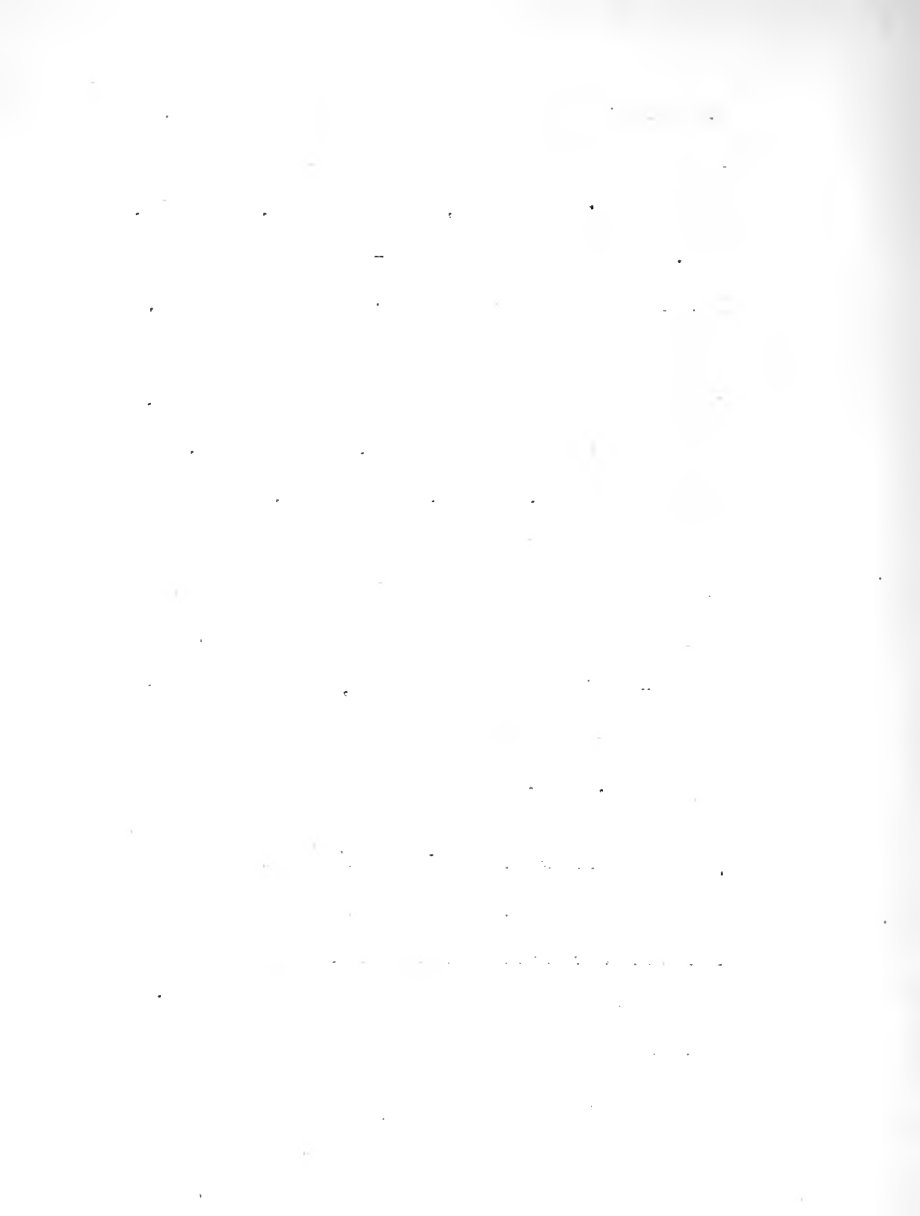
glue contains many recipes and formulae. In general the ingredients recommended are the alkaline earths, their salts, ammonia, etc. Formulae for water-resistant glues invariably recommend lime as the solvent, along with certain other additional ingredients to confer desirable properties, such as alkali carbonates, phosphates, sodium silicate, borax, arsenates, arsenites and an endless number of other ingredients to confer certain desirable properties. Formaldehyde is recommended to increase water-resistance qualities, sodium arsenate and caustic soda to improve adhesive strength, etc.

Section II - Preliminary

Experimentation

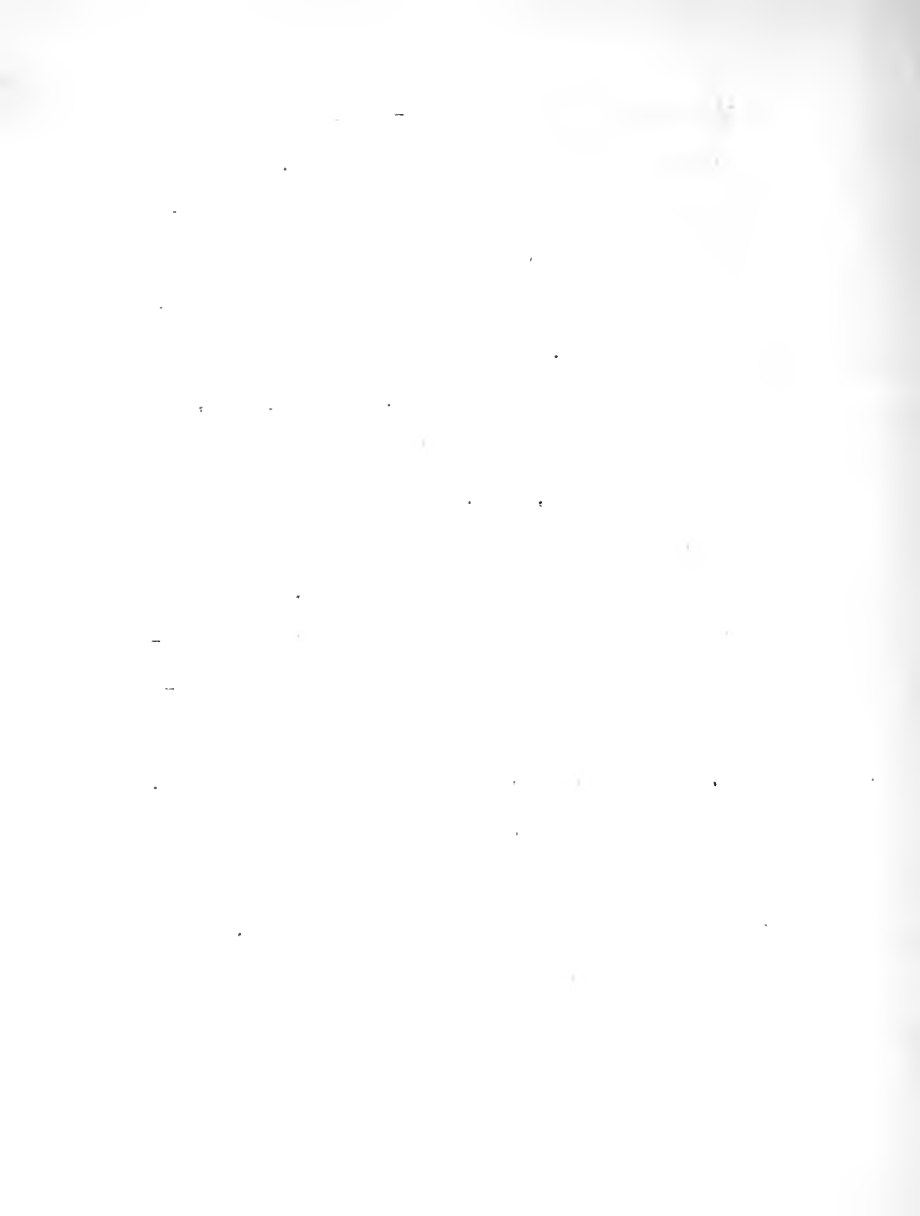
Early Experiments and Observations

For the purpose of acquiring familiarity with the behavior of casein under



the influence of the so-called "solvents" described in the foregoing text, a great number of experiments were performed using various proportions and combinations of the solvents with a suspension of casein in water. It became manifest early that solution of the casein particles was most rapid if a casein of fine mesh were employed, and, if the latter were allowed to soak for some time in water before mixing with the solvent. Since it was well recognized that promising results could be obtained from a glue prepared from lime and casein this simple combination served as the starting point.

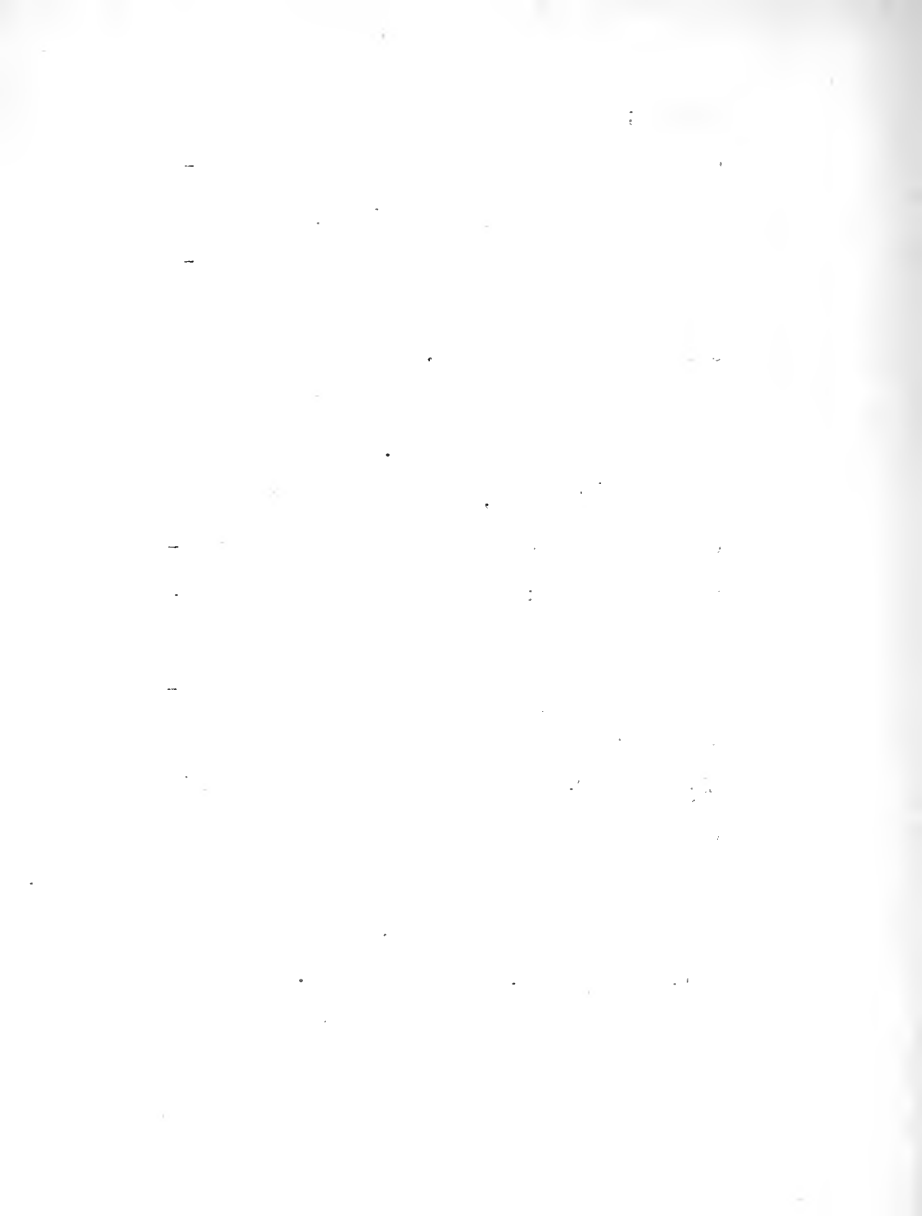
For this work there was available a number of technical caseins varying in quality from practically colorless, sweet smelling products through all gradations of color from light yellow to dark brown



bodies; some putrid from the rancidity of their high fat contents; others exhibiting sour and even highly offensive odors depending upon the degree of putrefaction developed as a result of careless manufacture. It was apparent at once that commercial caseins are far from uniform in quality.

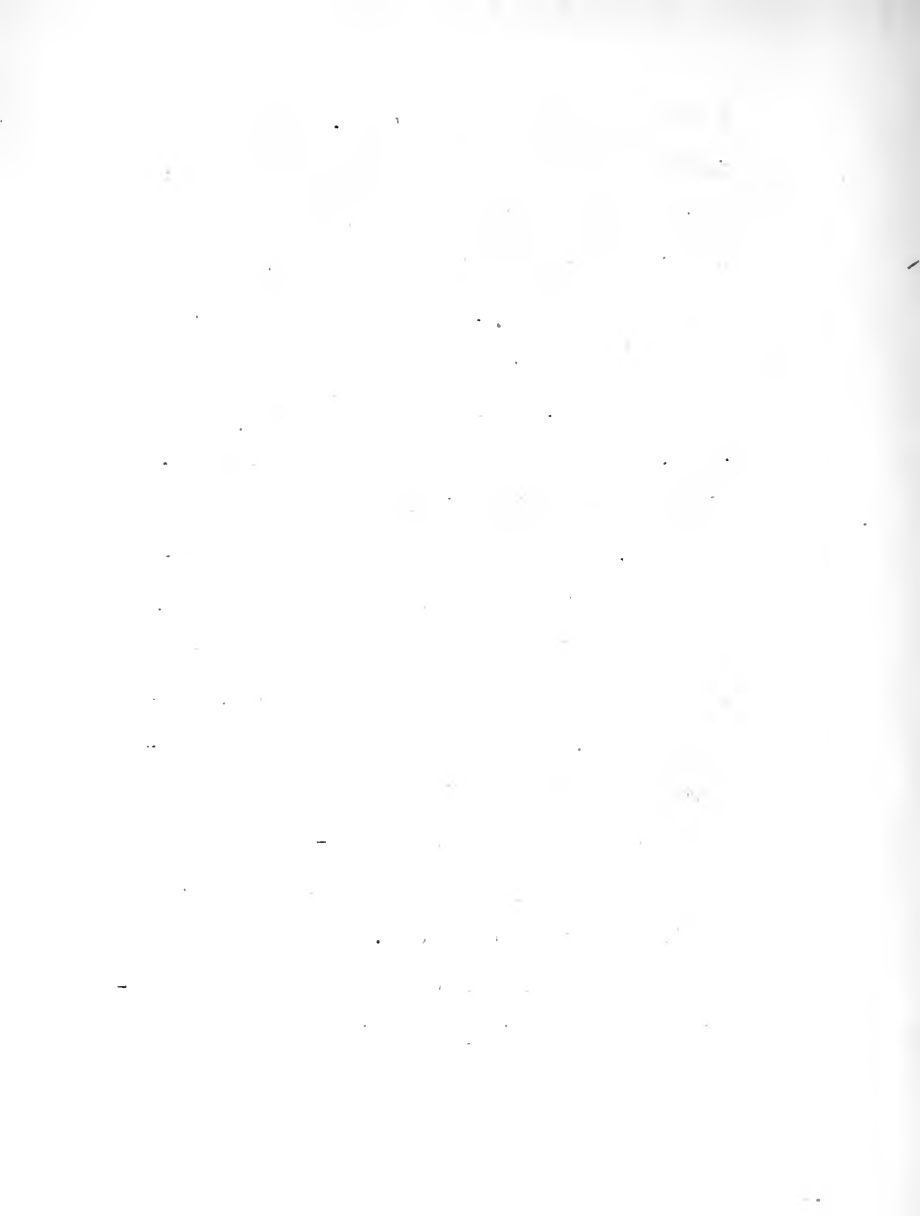
The caseins, sifted to a fineness of 20 to 40 mesh were soaked in a quantity of water; after some time the particles were observed to swell and absorb the free water producing a mush consistency which is hereafter designated as the "soak". Various proportions of milk of lime of different strengths were now stirred in and the agitation was continued until a uniform texture, practically free from particles, was obtained.

Sufficient water was added to produce



a ready flowing consistency. Under the influence of the lime (solvent) and proper agitation it was observed that the casein gradually disappeared into the body of the fluid, the latter developing at the same time a gradual increase in viscosity, a milky opalescent appearance, and marked mucilaginous qualities. These preparations invariably exhibited a rapid, spontaneous increase in viscosity with subsequent loss of fluidity and transformation into a rigid rubbery mass of no utility for the purposes under consideration. In general the range of usefulness (period during which preparation retained its fluid qualities-designated hereafter as "life") was exceeded in a period short of one hour.

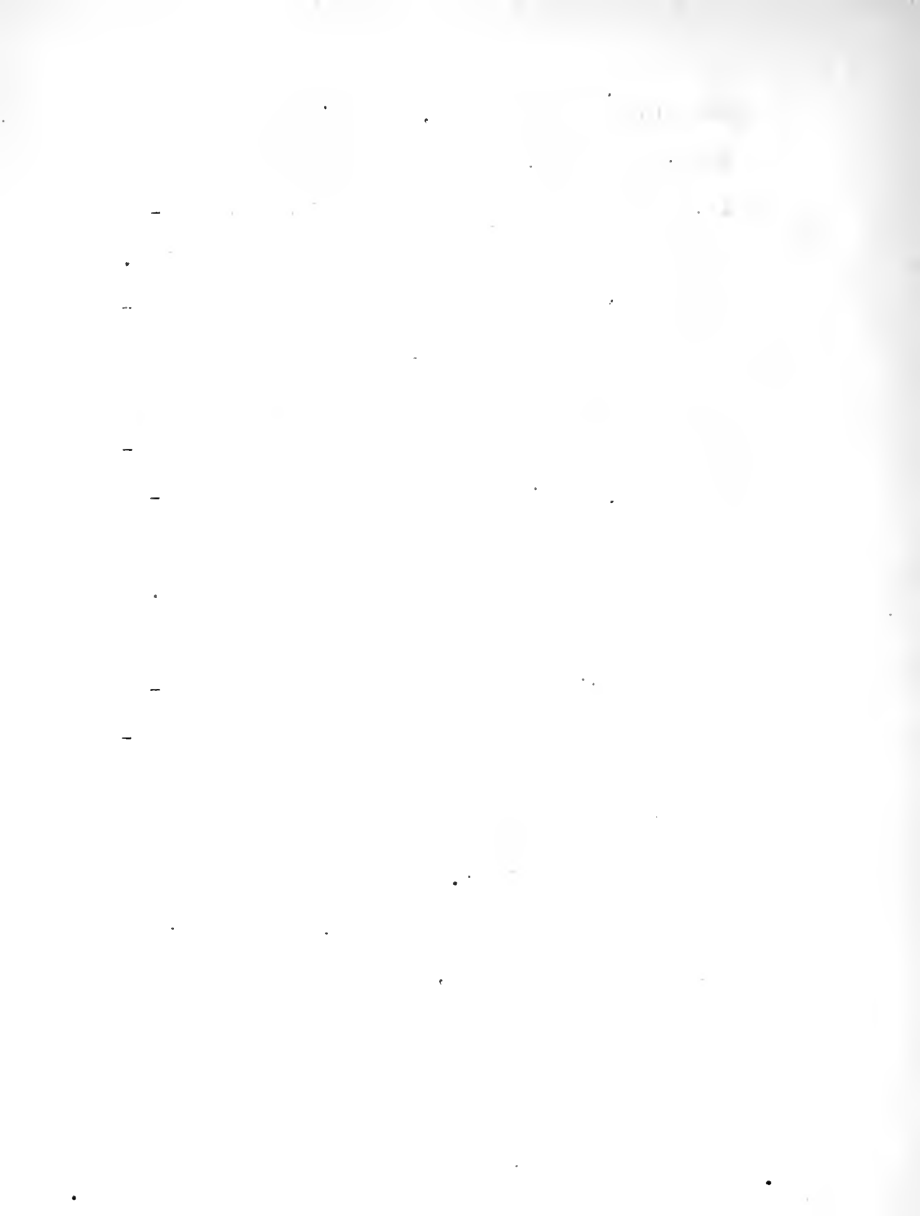
It was further observed that the glue-life decreased in proportion as the lime



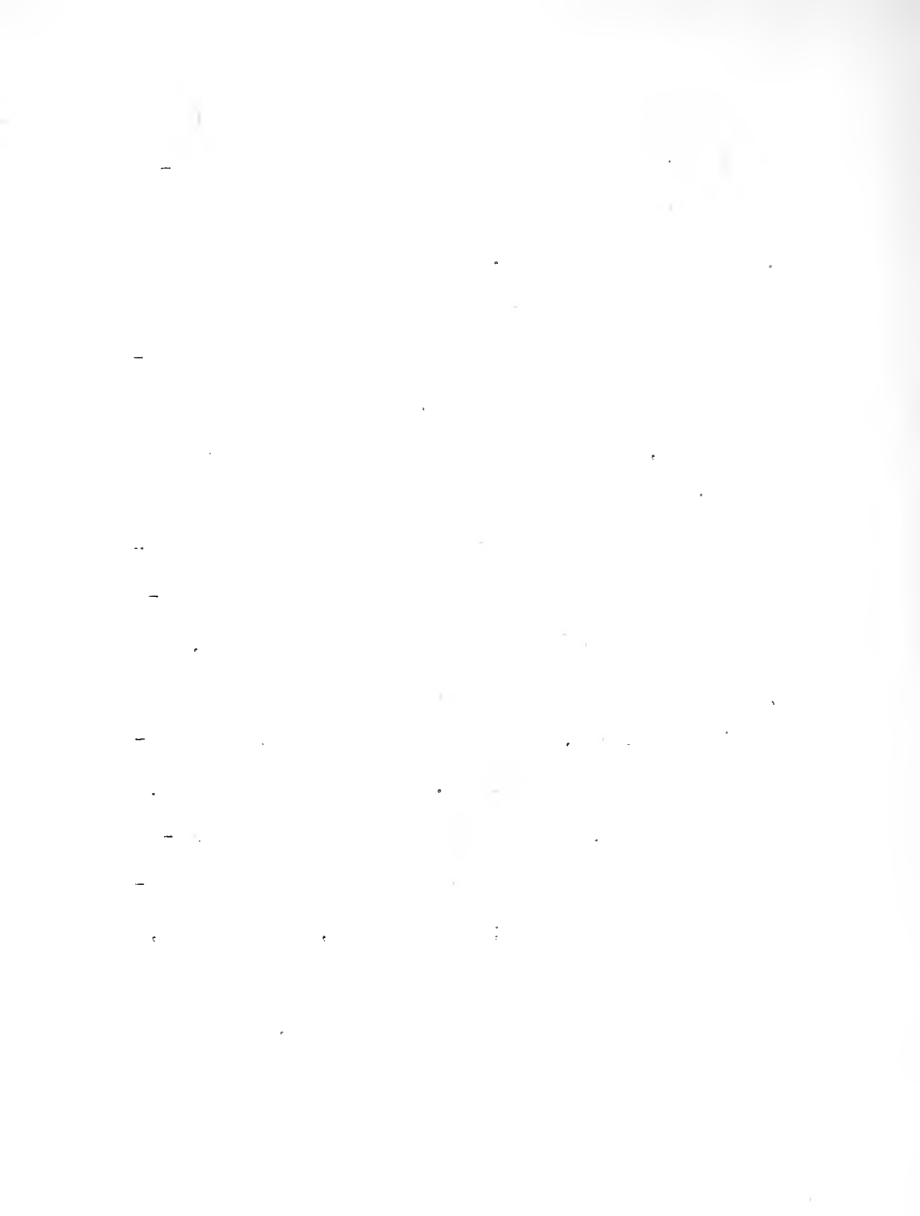
content was increased, notwithstanding the fact that repeated additions of lime invariably reduced the viscosity progressively and gave higher degrees of fluidity. Yet the minimum quantity of lime which served to cause proper solution of the casein did not produce an increase in life sufficient to prolong it beyond the extent stated above, without addition of such excessive quantities of water as to destroy most of the adhesive qualities of the mixture.

This very limited life was admittedly a very serious shortcoming of the casein-lime glues because in its commercial application the glue would exceed its period of usefulness in such a short time as to make its use impractical.

A very striking feature, which provoked much annoyance, as observed in the

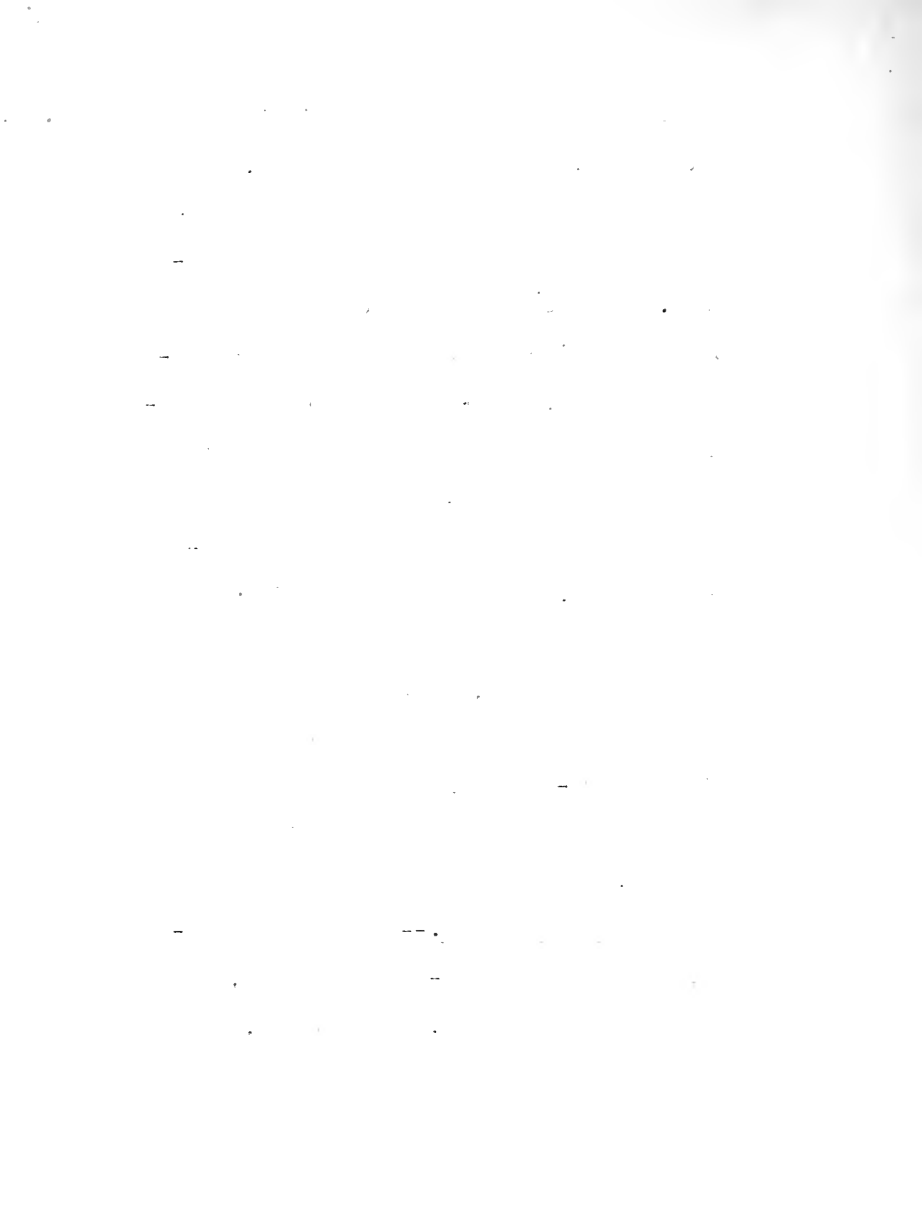


foregoing experiments was the enormous variation in viscosity developed by different caseins under the applications of the same formula. One casein yielded with a fixed quantity of water and lime a glue of satisfactory working consistency whereas the next casein tried might give a thick, heavy mixture of no utility because of low degree of fluidity. While this difficulty could be overcome by varying the quantity of water to meet the requirement of the specific casein used, the fact remained that technical caseins for some reason, differ widely in their water-absorbing capacities. This circumstance, obviously, would not admit of the evolution of a standard formula with fixed proportion of water; the latter, apparently, had to be determined for each new casein by some routine method of trial, unless



the cause underlying this variation were determined, on the basis of which, means for selecting caseins of a fixed water-absorption capacity would become available. This characteristic divergence in behavior of technical caseins so far experienced seemed to conform to the general impressions prevalent among commercial consumers of casein. One manufacturer will specify a preference for natural-sour casein, whereas another maintains that sulphuric acid casein only could serve his process, etc. No one seemed to have a conception of the reason for the difference - yet all were agreed that the behavior of technical caseins is far from uniform.

Interpretations.--The striking behavior of the casein-lime mixtures, the pronounced viscosity, opalescence, and



the rapid transformation of state from a fluid mixture to a rigid mass, none of which qualities are characteristic of true solutions, is conclusive evidence that the systems to be dealt with are emulsoid colloids of typically high viscosity, to which they owe their adhesive qualities. Reverting to the preliminary soaking of the casein, Robertson¹ points out that wet, freshly precipitated casein dissolves rapidly in the presence of solvents but the physical properties of dry, granular casein hinder solution. Experience has shown that if the casein particles are allowed to soak and swell in water they yield readily to the action of the lime, while if the dry granular casein were stirred up with lime and water a lumpy mixture obtains.

¹Robertson, T.B.- Physical Chemistry of the Proteids



This is entirely analagous to the fact that if gelatine is thrown into water and the mixture is immediately heated imperfect lumpy sols are likely to be obtained, while, if the gelatine is first allowed to soak and swell in water before heating, the process of solation occurs without trouble.

The literature reveals that casein dissolves in caustic alkalies forming transparent liquids which filter unchanged through porous earthenware. The writer has prepared such solutions with borax which are of low viscosity and remain fluid with no signs of setting for days. These give indication of a condition of true solution. In the case of the opalescent, highly viscous alkaline earth "solutions" of casein the situation is different. In the presence of calcium hydroxide, the casein, in

the language of colloid chemistry, probably adsorbs hydroxyl ions and dissolves. As more lime is added it follows, from the adsorption law, that more hydroxyl ions should be adsorbed - the degree of dispersity should increase; that is the size of particles should more nearly approach that of molecular subdivision and, accordingly, the viscosity should decrease. This was actually observed in the case of lime but is even more striking when caustic soda is used, small additions causing a material decrease in viscosity.

Another influence now begins to manifest itself - that of the powerful coagulating tendency of the divalent kation calcium. The system begins to exhibit its inherent instability, the extremely minute colloidal particles increase in size by coalescence, the viscosity increases spon-



taneously, the mixture becomes sluggish and gelatinization sets in, i.e., it "sets". This coagulation is irreversible and to this circumstance is attributed the ability of the glue to resist solvent action of water. As the calcium ion concentration increases the coagulating action becomes more powerful and, as observed, gelation takes place more quickly.

As a resume of the observations of the foregoing experiments two features are dominant, first, the diverse character of technical caseins and secondly, the inherent instability of the simple case-lime combination. The work immediately following was promptly undertaken with a view to investigate the first and to overcome the second.

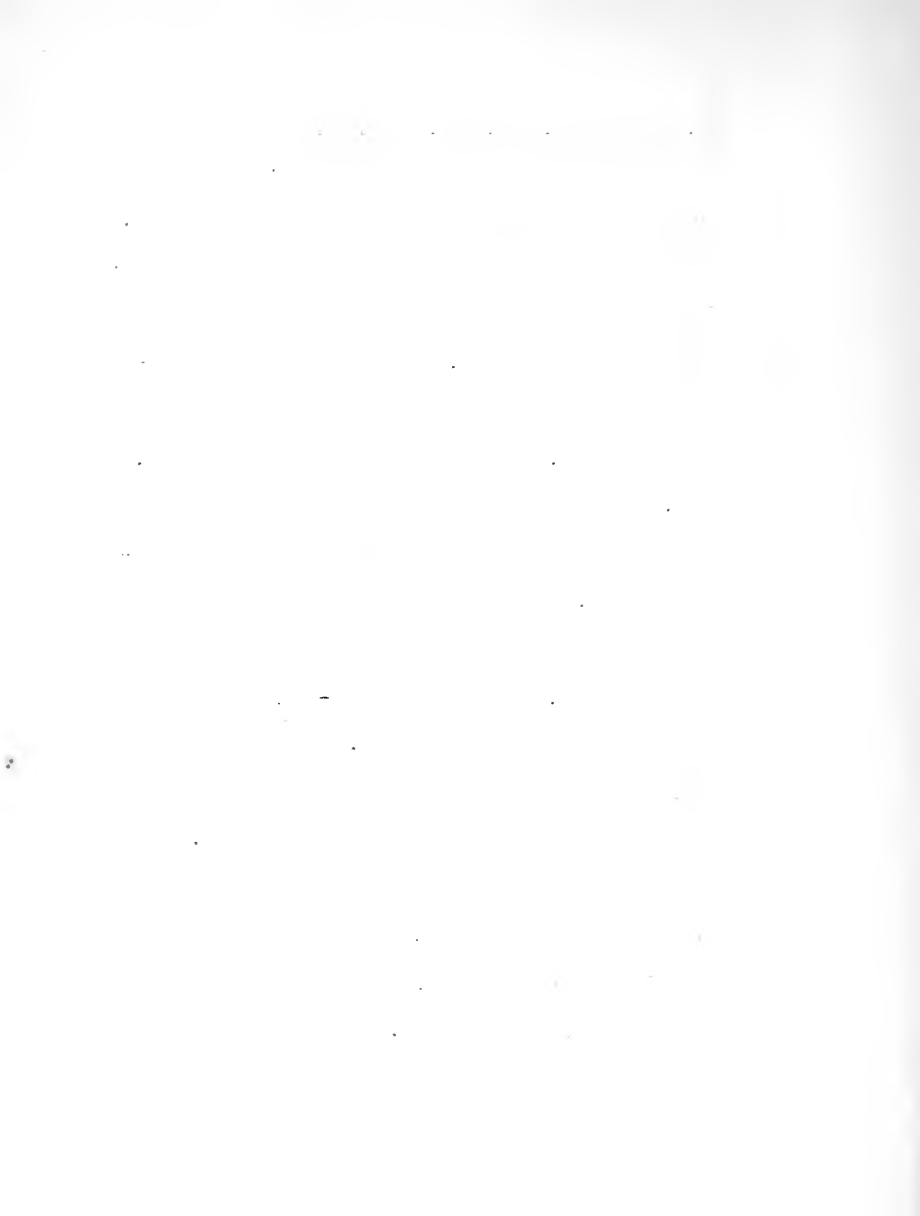


Preparation of Casein Samples

As an aid in determining the reason for the diversity in character of caseins, it was proposed to carefully prepare a series of caseins according to the various commercial methods, with the idea of correlating casein behavior with method of manufacture, factor affecting the latter, etc. The actual manufacture of the curd was performed at the University of Wisconsin dairy.

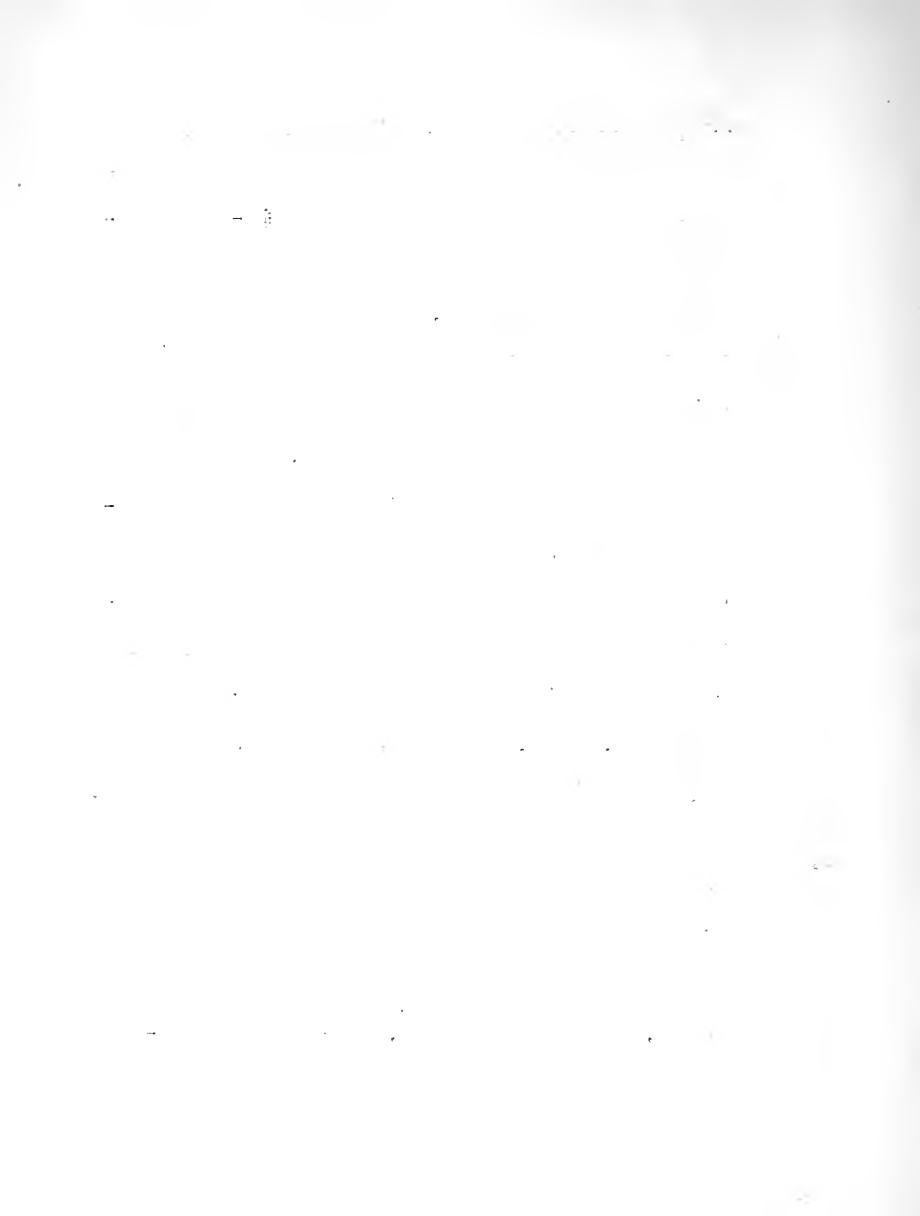
Caseins were prepared by the natural sour method, by the mineral-acid methods and by the rennet process. These were dried upon trays in a current of warm air and ground to flour in a pebble mill.

Actual examination of these caseins for glue qualities was deferred until a promising formula was developed as is subsequently described.



Stabilization of Casein - Lime Mixtures

Before undertaking any tests for water-resistance qualities of the casein-lime mixtures which had already demonstrated their inherent instability, steps were now taken to attempt to stabilize these mixtures in order to make them sufficiently practical to warrant further development. Inasmuch as the literature revealed no method of procedure it was decided to study the behavior of glues prepared according to the most promising of the many recipes available and to experiment with the use of gum arabic and gelatine, etc., because of their notorious stabilizing influence on colloidal solutions. To this end there was undertaken a prolonged series of experiments in which the simple casein-lime combination was incorporated with various proportions and combinations of borax, sodium carbonate, tri-sodium phos-



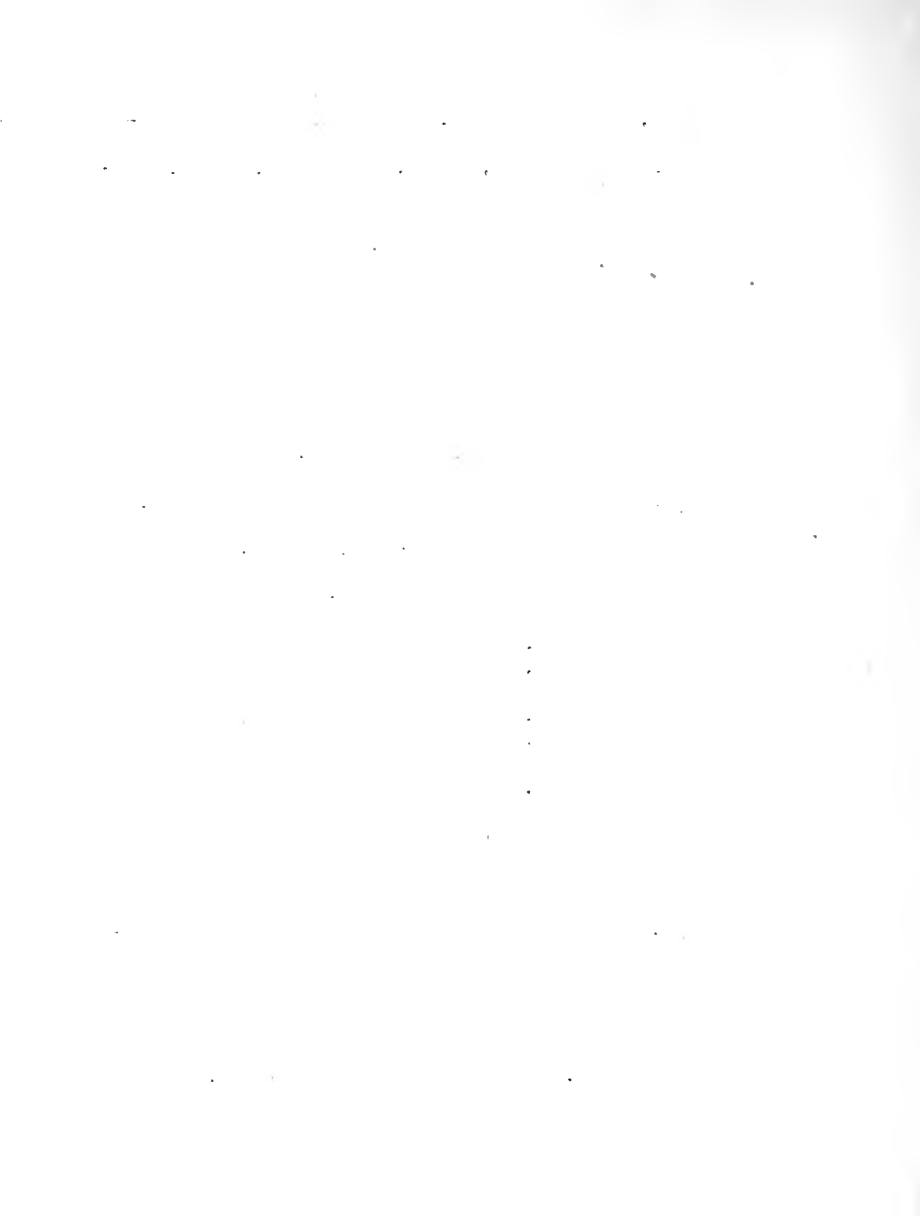
phate, caustic soda, ammonia, sodium silicate, zinc oxide, gums, gelatine, etc., following a tedious routine to exhaust possibilities.

As a result of the above work the very striking discovery was made that water glass exerts a material retarding influence on the gelatinization of casein glue. The formula used, giving ingredients and proportions, is given in formula VIII - #5, below.

Formula VIII - #5

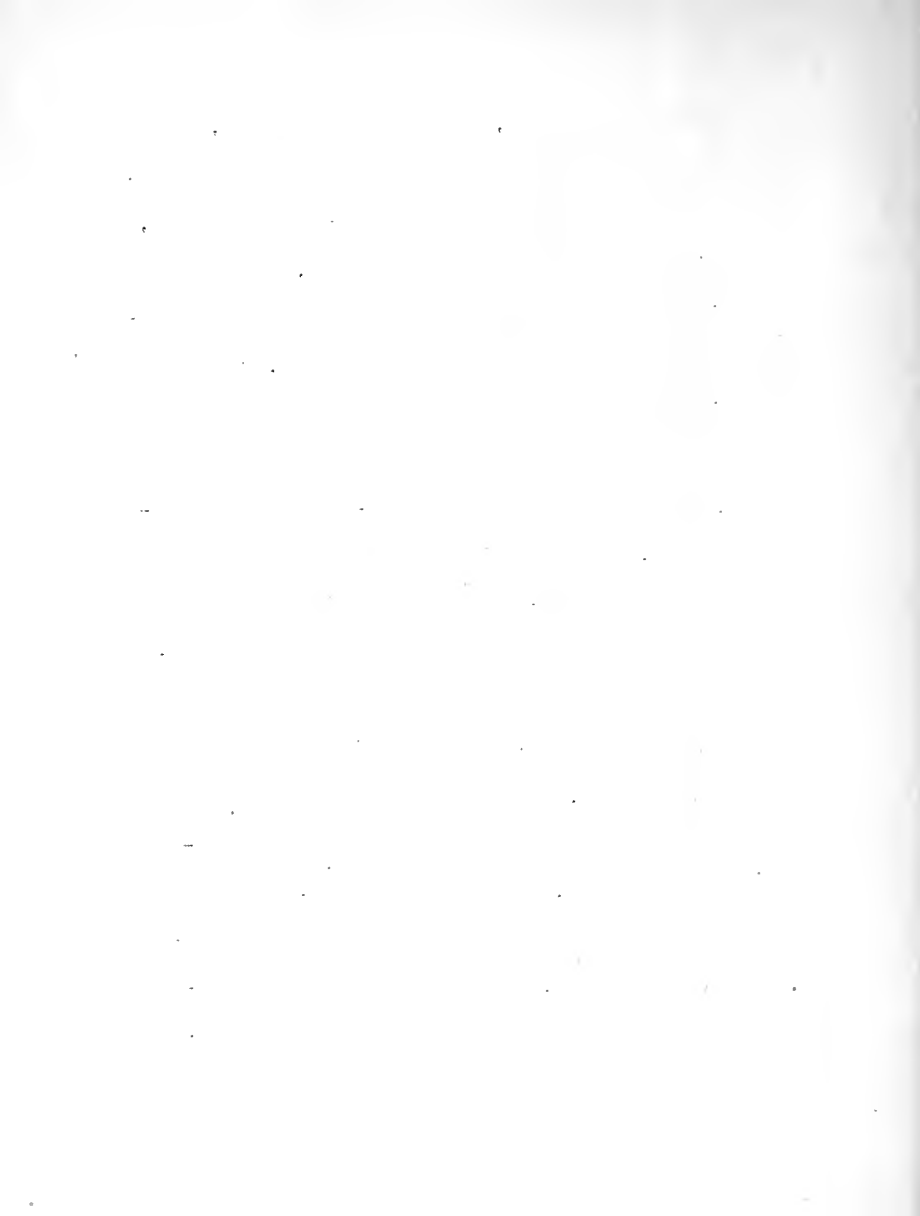
100 gr. casein)	Soak	
300 gr. water)	$\frac{1}{2}$ hour)	
+		
25 gr. CaO)		Mix)
125 gr. water)		Mix)
+		
50 gr. sodium silicate)		Mix

The casein was soaked in water for 1/2 hour following which the milk of lime was stirred in; after a few moments of stirring the water-glass was poured in and the agitation was continued until the mixture was free from lumps. These proportions gave, with



the casein used, a very watery fluid, which remained fluid for approximately 30 hours.

The fact that a casein-lime mixture, mixed practically as normally, had retained its fluid character for many hours by virtue of the addition of silicate, led to the idea of determining whether the retarding influence is dependent upon the stage of mixing at which the water-glass is introduced. It was first proposed to allow a simple casein-lime glue to increase in viscosity until a desirable working consistency was reached at which point the effect of introducing various amounts of "silicate", in the hope of maintaining this viscosity and fluidity for a prolonged time, would be studied. The next series of experiments were for the purpose of observing the effect of introducing various amounts of silicate im-



mediately after the lime had been stirred in.

The data obtained from the first procedure are given below in Table I.

Table I - Effect on Life of Stage of Introduction of Silicate

Proportions of Ingredients					
:Milk of:					
Casein:	Water:	Lime	Silicate	Life	
:	:	:	Amt.:	Time intro-	:
:	:	:	:	duced (after:	:
:	:	:	:	lime	:
gr.	gr.	gr.	gr.	min.	hrs.
100	300	(1-5) 150	52	40	2-1/2
100	300	150	25	60	3/4
100	300	150	60	60	1-3/4
100	300	150	52	75	1-1/2
:	:	:	:	:	:
:	:	:	:	:	:

The data from the second series of experiments, in which was studied the effect of increasing quantities of silicate introduced immediately succeeding the addition of lime

-

-

1. The first part of the document is a list of the names of the persons who have been appointed to the various offices of the city government. The names are listed in alphabetical order, and each name is followed by the name of the office to which the person has been appointed. The list is as follows:

Name	Office
John A. Smith	Mayor
James B. Jones	City Clerk
William C. Brown	City Engineer
Robert D. White	City Treasurer
Charles E. Green	City Attorney
Thomas F. Black	City Commissioner of Public Works
Henry G. Gray	City Commissioner of Health
John H. White	City Commissioner of Police
James I. Black	City Commissioner of Fire
William J. Gray	City Commissioner of Education
Robert K. White	City Commissioner of Public Safety
Charles L. Black	City Commissioner of Public Health
Thomas M. Gray	City Commissioner of Public Works
Henry N. White	City Commissioner of Health
John O. Black	City Commissioner of Police
James P. Gray	City Commissioner of Fire
William Q. White	City Commissioner of Education
Robert R. Black	City Commissioner of Public Safety
Charles S. Gray	City Commissioner of Public Health
Thomas T. White	City Commissioner of Public Works
Henry U. Black	City Commissioner of Health
John V. Gray	City Commissioner of Police
James W. White	City Commissioner of Fire
William X. Black	City Commissioner of Education
Robert Y. Gray	City Commissioner of Public Safety
Charles Z. White	City Commissioner of Public Health

are given in Table II. The formula employed was the same as that used above save that the silicate was varied as shown; the corresponding life is also shown.

Table II - Effect of amount of Silicate on Life

Casein:		Silicate:		Life
gr.	:	gr.	:	hrs.
100	:	25	:	1-3/4
100	:	36	:	5
100	:	52	:	30
100	:	58	:	32

Analyzing the data from Table I and Table II the following features are dominant:

1. Gelatinization of casein-lime mixtures is delayed by the presence of silicate; the extent of the retarding influence is actuated by the stage of mixing at which the silicate is introduced.
2. The retarding influence is effective

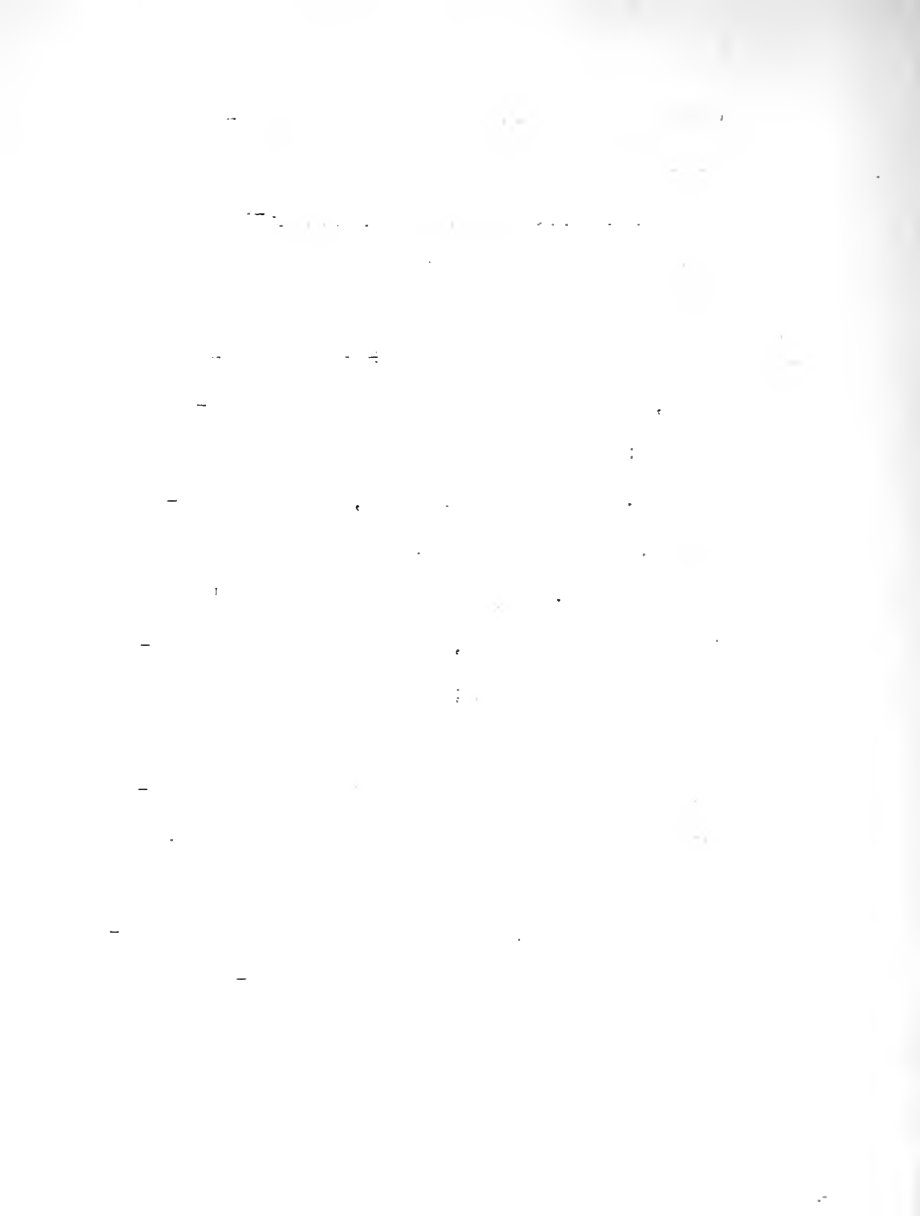


only if the silicate is added immediately after the lime.

Mechanism of Stabilization.--

With regard to the explanation of the retarding influence of silicate upon the gelation of the casein-lime mixture, two possibilities present themselves:

I. Emulsoid colloids, such as silicate, have a tendency to "protect" less stable sols. According to Bechhold's idea of protection, the latter is the result of adsorption; a thin layer of the silicate is adsorbed at the interface and thus confers its stability on the adsorbing particles of calcium caseinate. The latter are thus effectively prevented from forming aggregates until the relatively stable silicate membrane gels - hence gelation of the mixture is itself delayed



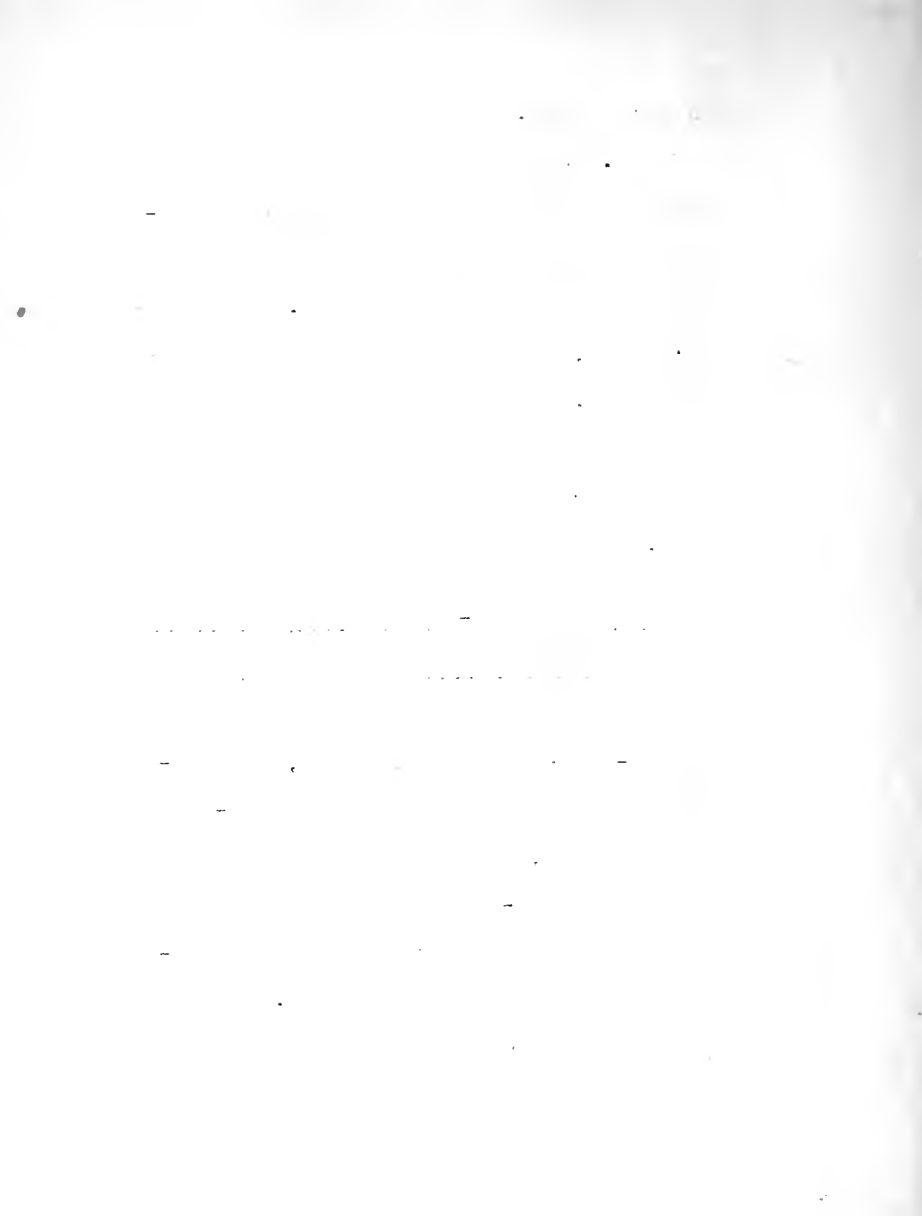
to this point.

II. Another possibility is that the silicate maintains a very low concentration of calcium ions through formation of insoluble calcium silicate. This circumstance, obviously would slow down coagulation.

It is of course possible that both actions described may be in operation at once.

Section III - Investigation of Glue Qualities of Silicate Mixtures

In view of the promising aspect of casein-lime-silicate mixtures, particularly as combined in formula VIII - #5 (preceeding), it was next in order to test the water-resistance and strength qualities of this combination to determine the degree of its utility. For this purpose the following series of routine



tests were to be applied.

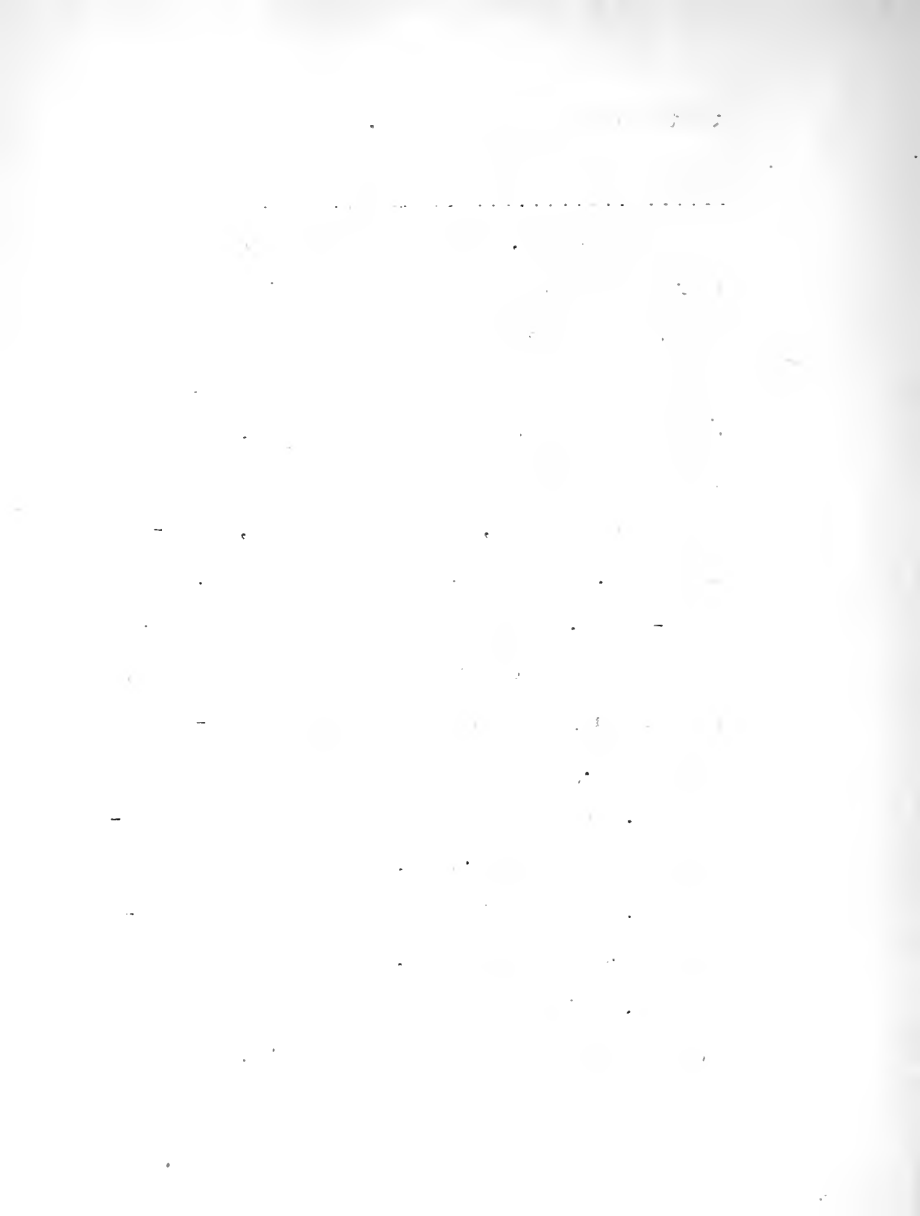
Methods of Testing Glue Qualities

Obviously, rational tests for the determination of glue capabilities must be such as determine whether glued joints will effectively resist the deteriorating conditions encountered in service. Glued joints in aircraft service must contend with fresh water, lubricating oil, gasoline and, in the case of hydroplanes, with Salt-water. To study the relative severity of these conditions the following tests had already been completed on veneer-panel specimens.

1. Soaking in fresh water at room temperature for two weeks.

2. Soaking in salt water at room temperature for two weeks.

3. Boiling in fresh water for 24 hours followed by baking at 212°F. for 24



hours.

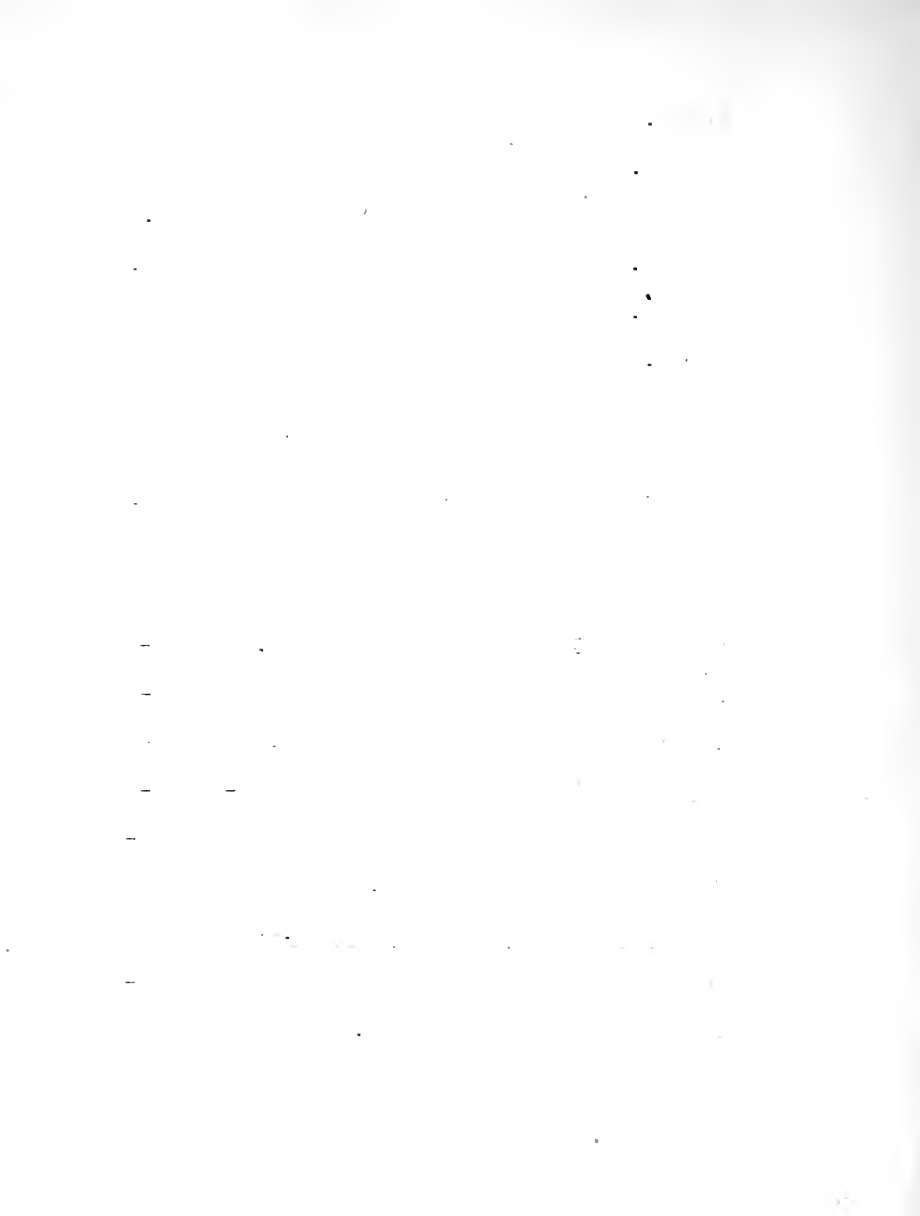
4. Boiling in salt water for 24 hours followed by baking at 212°F for 24 hours.

5. Soaking in gasoline for one month.

6. Soaking in gas engine oil for one month.

The result of these tests showed that panels soaked in gasoline or gas engine oil withstood the action of these substances better than if soaked in fresh water and that salt water had the same effect upon the glue as the fresh water. Specimens which withstood the boiling test invariably passed the baking test. Accordingly the tests retained for water-resistance qualities were the boiling and soaking tests in fresh water.

Boiling and Soaking Tests.--Panels to be tested were cut into specimens approximately five inches square. It was found that specimens which withstood 8 hours



boiling also withstood 24 hours boiling, hence for inspection purposes the eight hour boiling test was adopted. It was also determined that a specimen which withstood 8 hours boiling would apparently withstand two weeks soaking in cold water. Hence the boiling test was considered in the nature of an accelerated soaking test, and, as an identical criterion, it was used in place of the soaking test because it could be very quickly completed.

The panels for test were made up of 1/16 inch veneer (generally birch faces and poplar core) glued, retained under pressure overnight and dried at 110°F. for 24 hours.

The designations adopted for the expression of results of the water-resistance tests on plywood specimens are given below:



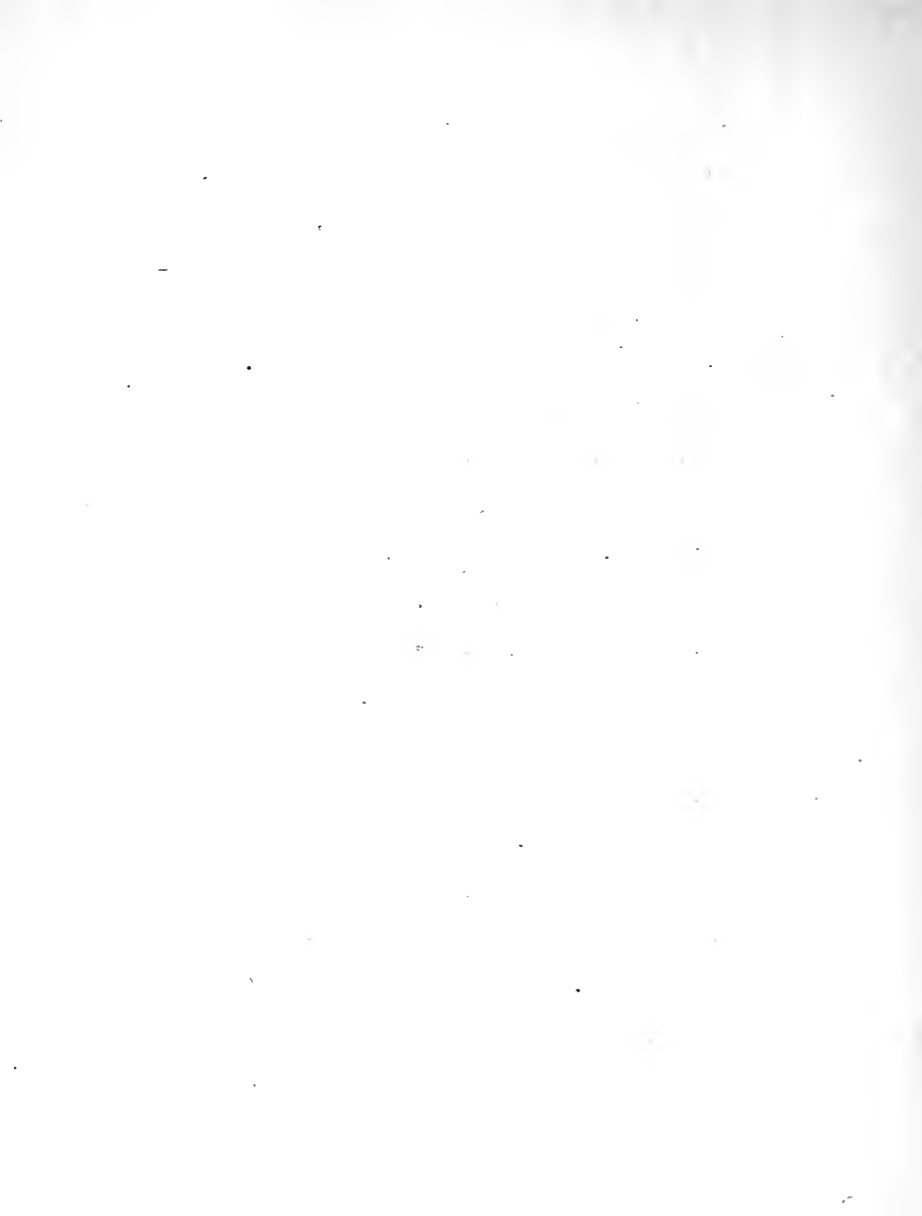
<u>Designation</u>	<u>Condition Corresponding</u>
--------------------	--------------------------------

- | | |
|---|--|
| A | Indicates no separation of the plies. |
| B | Indicates that the total separation between all the plies, regardless of the number of plies, is not greater than 10 per cent of the area of sample tested. |
| C | Indicates a total separation greater than 10 per cent and not more than 50 per cent of the area of sample; or indicates blisters or other manufacturing defects of such nature as would warrant further tests. |
| D | Indicates a total separation of over 50 per cent of the area of sample tested. |

Test for Adhesive Strength.--The test for adhesive strength was made on a test specimen of the form and dimensions shown in Fig. 3. These specimens were made of maple having a shearing strength of approximately 2400 pounds per square inch. This requires wood having a dry weight of about

50 pounds or more per cubic foot and a moisture content of 8 to 12 per cent. After gluing the test blocks, (from which the test specimens are subsequently cut) these were held in clamps under pressure for about 16 to 24 hours. They were then released from the clamps and allowed to stand for six additional days in order to dry and develop maximum strength. The test specimens were then cut to conform to Fig. 3 and tested in a standard Olson machine equipped with a special jig (shown in Fig. 4) to deliver a downward force against one member of the joint while the other rested upon a fixed platform.

This test is hereafter referred to as compression shear test or - simply shear test.



Test and Development of Formula VIII - #5

In the examination of formula VIII - #5, given below, it was decided to neglect the tests for adhesive qualities in this preliminary analysis until the proportions had been so adjusted as to give a glue of proper working qualities and consistently satisfactory ability to pass the boiling test.

100 gr. casein)	Soak	
300 gr. water)	1/2 hour)	
+)	
25 gr. CaO))	
125 gr. water))	
+)	Mix
50 gr. silicate)	

On preparation, the glue showed a very fluid consistency. Test panels of 1/16 inch stock (birch faces on poplar core - 3 ply) were made at intervals, as shown below, throughout the life of the glue (29 hours). These panels when tested gave consistently

satisfactory results, viz:-

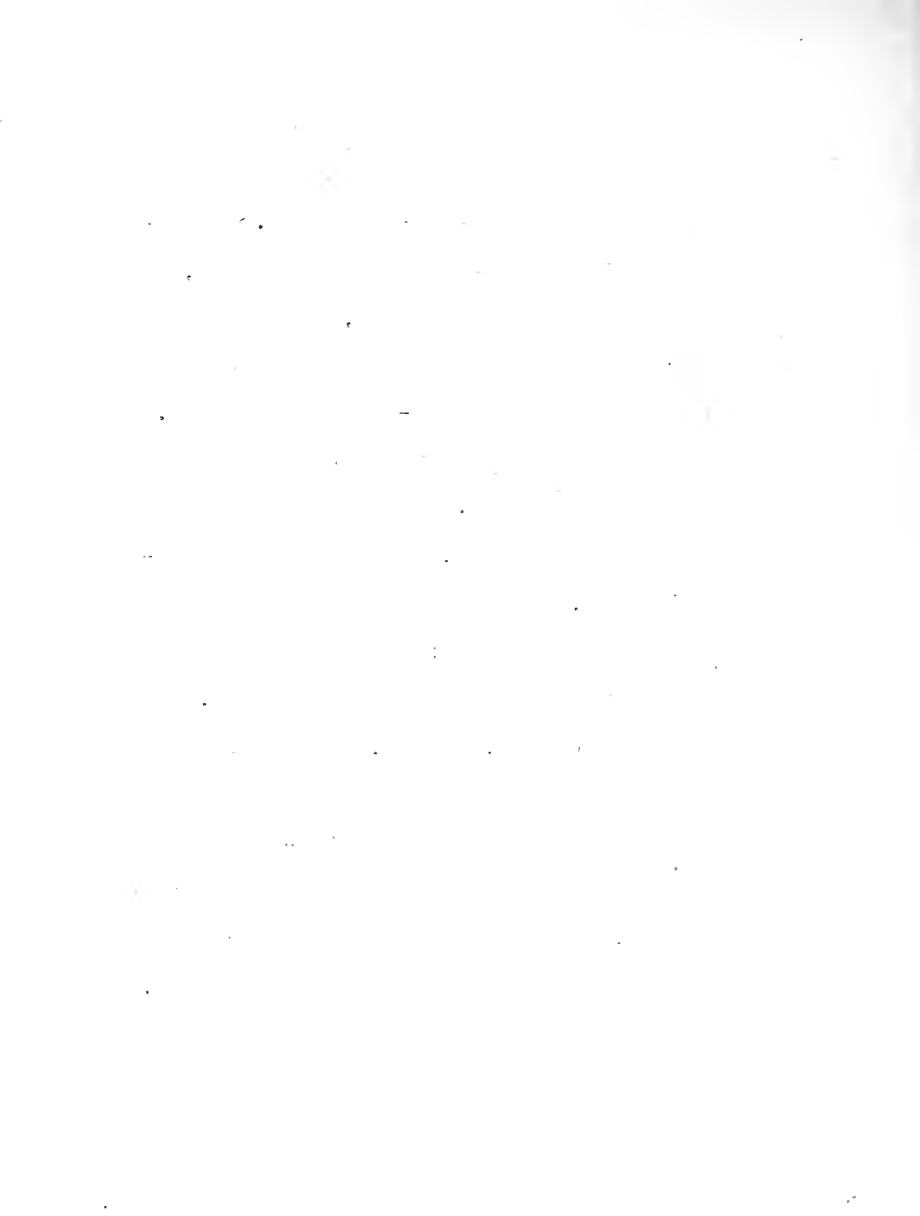
<u>Age of Glue When Tested</u>	<u>Boiling Test</u>
0 Hrs.	A
1 "	A
1-1/2 "	A
3 "	A
4 "	A
6 "	A
7 "	A
8-1/2 "	A
22 "	A
24 "	A
26 "	A
27 "	A
29 "	A

On account of the too fluid character of the above glue the silicate was reduced to 40 grams per 100 of casein. The silicate was manipulated rather than the water in order to reduce cost. This gave



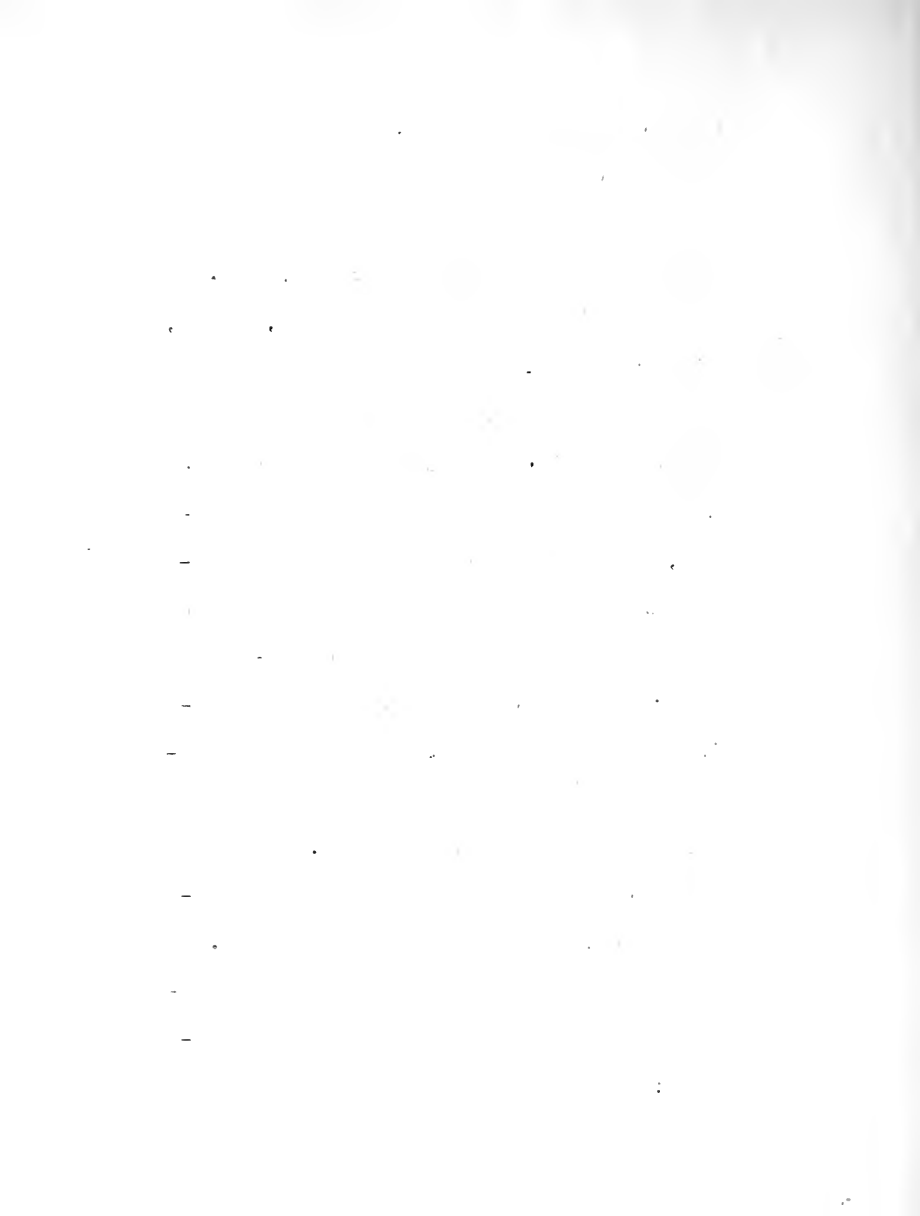
a glue of slightly higher viscosity which passed the boiling test satisfactorily but showed a life of but 7-1/2 hours. In order to further increase the viscosity, so as to improve adhesiveness, it was decided to manipulate the lime this time so as not to jeopardize the glue-life any further. The lime was then reduced to 20 parts of CaO in place of 25. The result was a glue of higher viscosity, greater apparent adhesiveness, and of equally satisfactory ability to pass test; its life was increased to 13 hours by the reduction of lime.

The formula, by now, had apparently matured to the point where it measured up fairly satisfactorily to water-resistance requirements when applied to the one casein used. It was next in order to apply the formula to a series of other caseins. The store of lime originally drawn upon



had now been exhausted. Its analysis was unknown yet from its behavior and appearance it was seen to be very much air slacked and probably carbonated. The new lime was much "quicker", hence, higher in CaO. Since adherence to the old proportions of 20 parts lime per 100 of casein would lead to the introduction of more actual CaO than intended, this difficulty was corrected approximately by reducing this figure to 25 parts per 200 of casein or $12\frac{1}{2}$ parts per 100 of casein. This approximate procedure was considered justifiable inasmuch as the modifications so far made were all very crude. The water used for slaking the lime was also reduced to 90 parts per 100 of casein.

The modification of formula VIII - #5 now presented the following appearance:



Formula VIII - #10

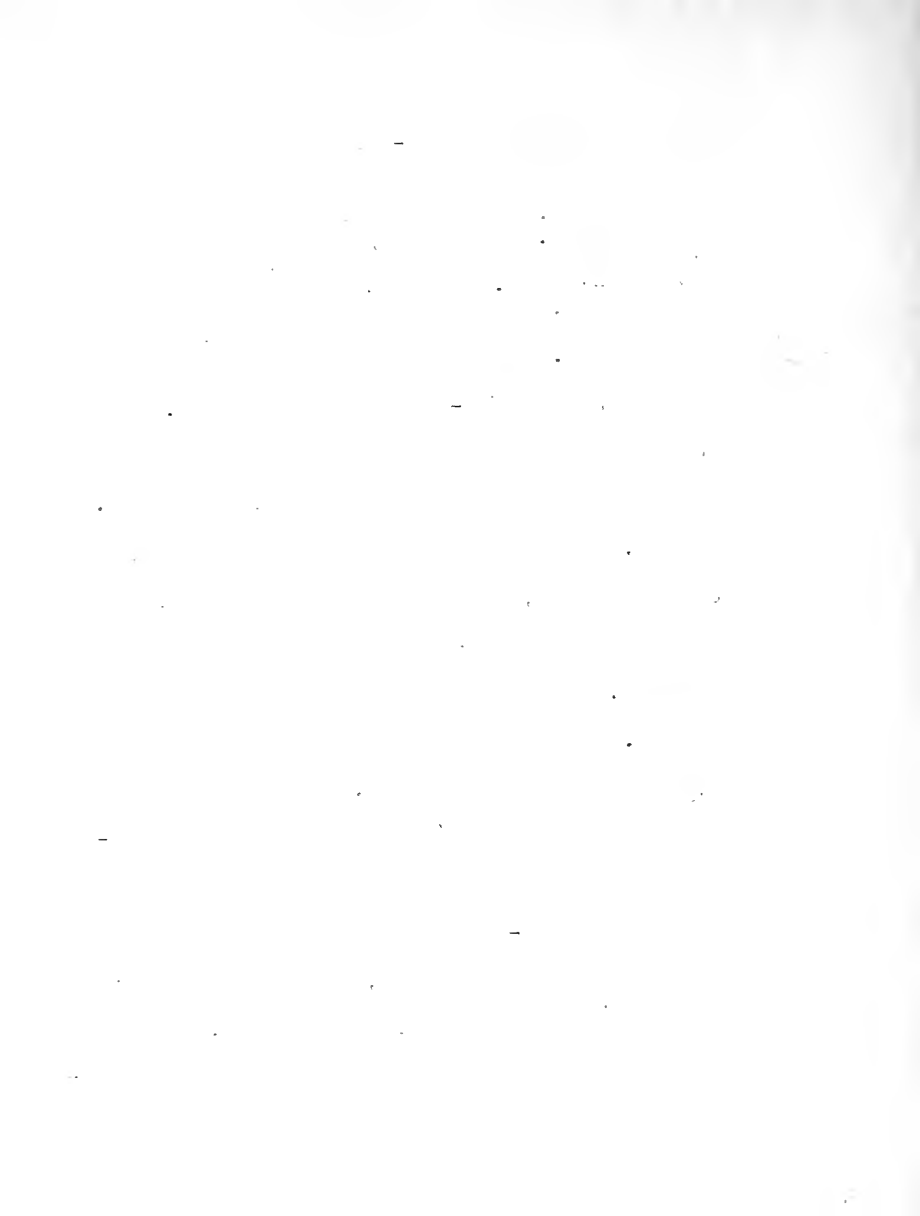
100 gr. casein)	Soak	
300 gr. water)	1/2 hour)
	+		
12-1/2 gr. quicklime))
90 gr. water))
	+)
40 gr. silicate)		Mix

Formula VIII - #10 as given above, was now applied to a series of caseins from the behavior of which two features predominated.

1. The viscosities lacked any display of uniformity, testifying again to the great diversity in water-absorption abilities of caseins.

2. The life of the various preparations averaged but 4 to 5 hours.

The remedy proposed was to omit any reference in the formula to the proportion of soaking water - the latter to be determined for each casein by trial, until further information became known. For case 2, the lime and silicate were both manipulated in a direc-



tion which would increase the life. This led to the evolution of Formula No. 3.

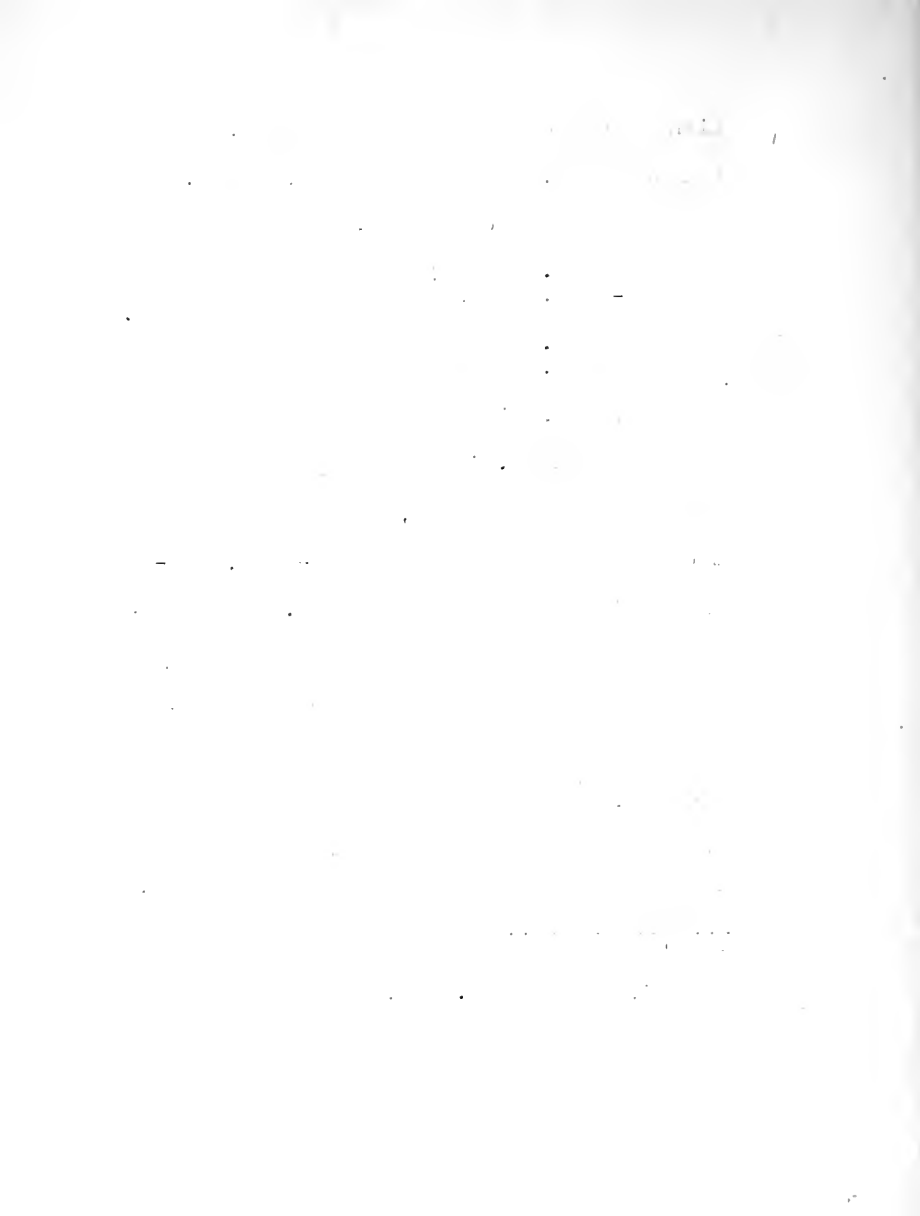
Formula No. 3

100 gr. casein)	Soak	
- 1 gr. water)	1/2 hour)	
+)
8 gr. CaO^2)))
90 gr. water)))
+) Mix
70 gr. silicate)

Formula No. 3 was now applied to the same series of caseins, which included those prepared by the natural-sour, mineral acid and rennet processes. The soaking water was in each case determined by trial as that quantity required to produce a viscous mixture of high adhesive quality. All of the glues passed the boiling test satisfactorily. Rennet casein required an abnormally large quantity

1 Proportions to be determined by trial

2 Equivalent to 10.6 gr. $\text{Ca}(\text{OH})_2$



of water to produce the desired consistency; 280 parts of water were used for 100 parts of casein, or expressed as a ratio by weight of casein this equals 2.80.

Section IV - Development of the Glue Formula

Proving of Formula No. 3

Glue No. 3 having presented promising aspects on application to a limited number of caseins, it was proposed to apply it to a wider range of caseins, whose histories of manufacture were known, in order to determine the possibilities of the formula. It was also hoped that reasons for the diverse character of caseins might become apparent from the data derived.

Caseins Used.--Through the cooperation of Mr. Dahlberg of the Bureau of Animal Industry, a series of caseins of a diversified

nature were prepared at the Grove City (Pa.) Creamery and forwarded to the Laboratory for use in the following investigation. In all, 25 caseins were studied, among them being a lactic casein prepared by the writer, and a lactic casein obtained from the Knowles Creamery, Knowles, Wis.

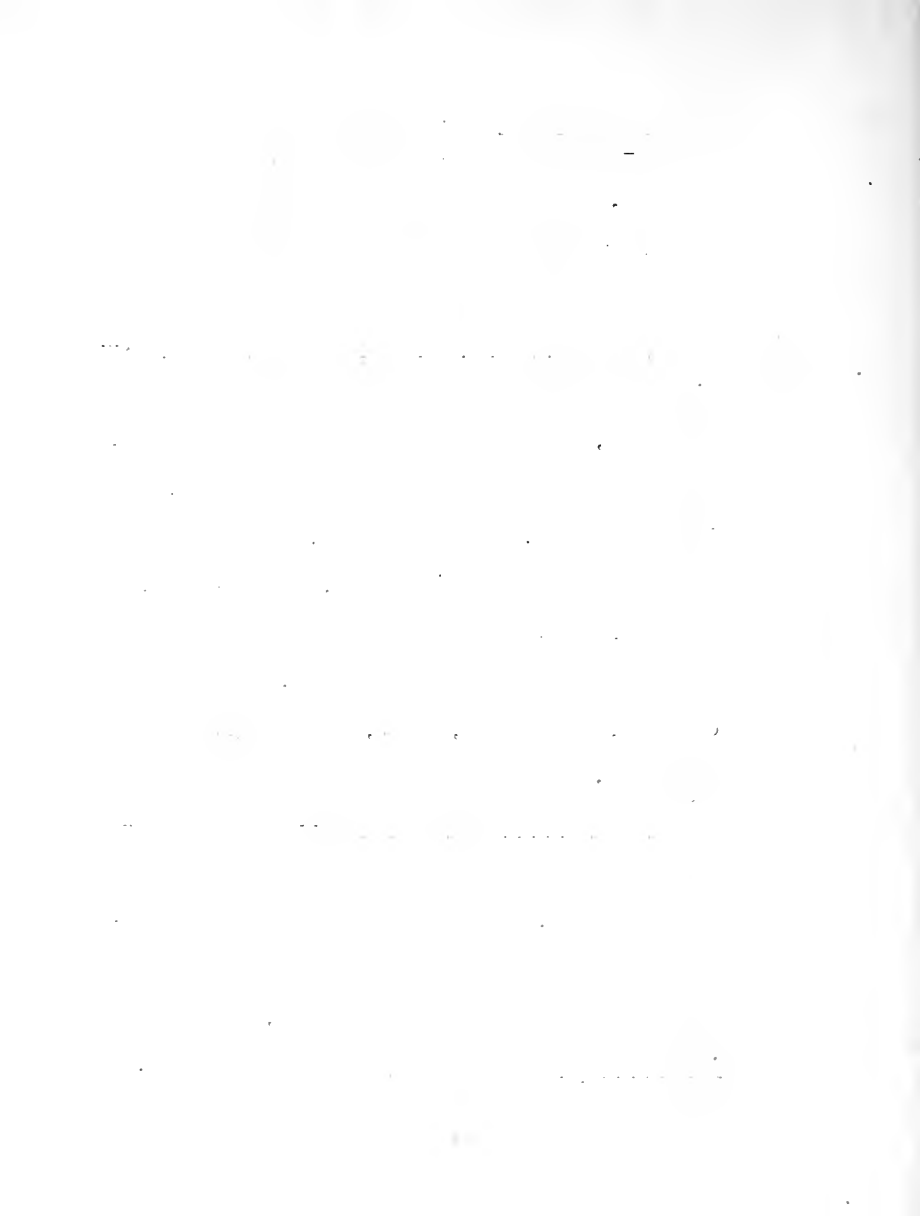
General Formula Employed.--Each casein was prepared in the form of a glue according to formula No. 3 below, observing the necessary precautions regarding water requirement. In a few instances the glue viscosity for the same casein was varied by changing the water content, in order to determine what limit of water content must be exceeded in order to make manifest a significant depreciation of properties.

100 parts casein)	Soak	
- 1 parts water)	1/2 hour)	
+)
10.6 parts powdered))
hydrated lime)))
90 parts water))) Mix
+)
70 parts silicate)

Preparation and Testing of Specimens.--

Within one hour after the preparation of the glue, the test specimens were prepared. These consisted of a veneer panel twelve inches square, made up of 1/16" birch faces and 1/16" poplar core, and two maple shear blocks. These specimens were aged and tested in the usual manner. The length of life, viscosity, etc., of the glue were recorded.

Results and Discussion.--The data derived from the above procedure are recorded in Table III. From its review there is indication that caseins derived from ordinary standard methods of manufacture, with the possible exception of buttermilk caseins, 1-proportion water to be determined by trial



can be made to pass the boiling test satisfactorily by a mere variation of the amount of soaking water. From the consistent failure in the soaking test, however, the formula is unsatisfactory. It is to be noted in this regard that the interchangeability of these two methods of test for water-resistance quality can no longer be considered as unqualified, identical criteria.

It is interesting to note that while water absorption capacity¹ has heretofore been observed to vary widely between the limits of the range 1.3 to 2.8, the tabulated data indicates very strikingly the possibility of classifying caseins so as to bring these limits closer together. For lactic acid casein the ratio - soaking water to casein by weight - varies

¹ Ratio of soaking water to casein by weight.

10

in the range 1.35 to 1.7; for mineral-acid casein in the range 1.7 to 2. plus; for rennet casein previous work shows the ratio has a value about 2.8. In other words the water absorption capacity is dependent on some influence of the method of manufacture.

Examining into the influence of viscosity upon the various glue properties in order to observe the extent to which necessity for high viscosity exists, it is seen that low viscosities tend to show inferior results in water-resistance qualities as well as strength. A relatively thick consistency, aside from inconvenience of handling, seems more desirable. The strength of the glue, when viscous mixtures are used, appears to average 2400# / in.², comparing favorably with high grade animal glue.

1. The first part of the paper is devoted to the study of the properties of the function $f(x)$ defined by the equation

$$f(x) = \int_0^x \frac{1}{1+t^2} dt.$$

2. It is well known that the function $f(x)$ is increasing and concave down on the interval $(-\infty, \infty)$.

3. The second part of the paper is devoted to the study of the properties of the function $g(x)$ defined by the equation

$$g(x) = \int_0^x \frac{t}{1+t^2} dt.$$

4. It is well known that the function $g(x)$ is increasing and concave up on the interval $(-\infty, \infty)$.

5. The third part of the paper is devoted to the study of the properties of the function $h(x)$ defined by the equation

$$h(x) = \int_0^x \frac{t^2}{1+t^2} dt.$$

6. It is well known that the function $h(x)$ is increasing and concave down on the interval $(-\infty, \infty)$.

7. The fourth part of the paper is devoted to the study of the properties of the function $k(x)$ defined by the equation

$$k(x) = \int_0^x \frac{t^3}{1+t^2} dt.$$

8. It is well known that the function $k(x)$ is increasing and concave up on the interval $(-\infty, \infty)$.

9. The fifth part of the paper is devoted to the study of the properties of the function $l(x)$ defined by the equation

$$l(x) = \int_0^x \frac{t^4}{1+t^2} dt.$$

10. It is well known that the function $l(x)$ is increasing and concave down on the interval $(-\infty, \infty)$.

11. The sixth part of the paper is devoted to the study of the properties of the function $m(x)$ defined by the equation

$$m(x) = \int_0^x \frac{t^5}{1+t^2} dt.$$

12. It is well known that the function $m(x)$ is increasing and concave up on the interval $(-\infty, \infty)$.

13. The seventh part of the paper is devoted to the study of the properties of the function $n(x)$ defined by the equation

$$n(x) = \int_0^x \frac{t^6}{1+t^2} dt.$$

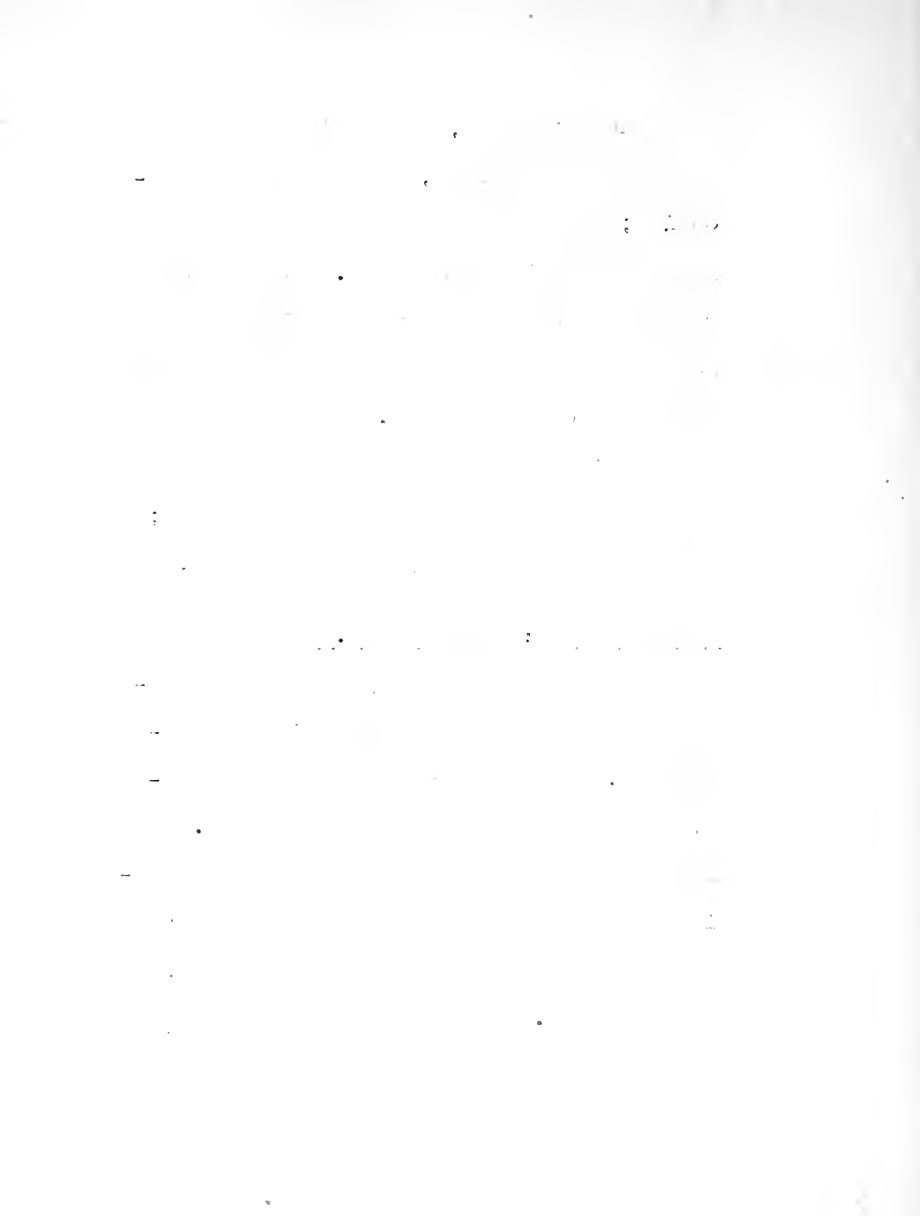
14. It is well known that the function $n(x)$ is increasing and concave down on the interval $(-\infty, \infty)$.

The glue life, for a fixed quantity of lime and silicate, depends on the viscosity; low viscosities yielding a longer life than high viscosities. Low viscosity mixtures are seen to attain a life of 90 hours whereas high viscosity mixtures show a life of only 20 hours.

It is to be noted that no one type of casein seems more desirable than others; all appear to be equally satisfactory.

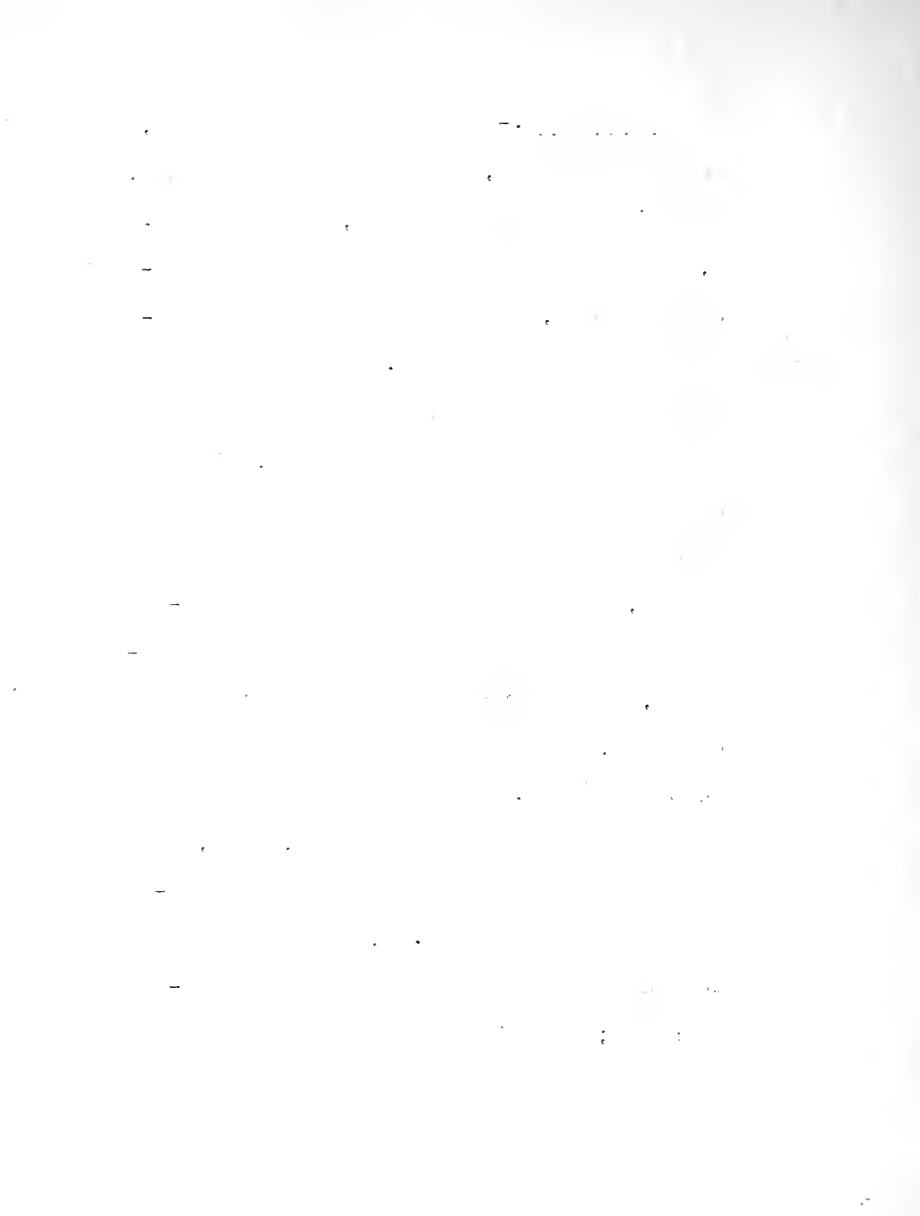
Modification of Formula No. 3

In spite of the many desirable features of glues prepared according to Formula No. 3 the latter was absolutely unsatisfactory for the purpose in mind. Yet it was felt that the formula could be manipulated to pass the requirements of the soaking test by resorting to some simple modification.



Procedure.--The method of procedure, for modification, was based upon the fact, already known for sometime, that Glue No. 3, prepared without the addition of silicate of soda, passed the cold water soaking test satisfactorily. From this it had been assumed that the silicate acts counter to the calcium caseinate, either by reacting with some of the lime and hence depriving the casein of lime to this extent, or else by the action of peptization. If the latter is the true explanation, and if such action could not be overcome, the use of silicate would have to be rejected.

Working on the assumption, then, that an insufficient quantity of lime is prescribed in formula No. 3, it was proposed to increase the lime content by two increments; the first modification was to



use 13 parts lime per 100 of casein, the second - 15 parts. These two modifications were to be applied to various caseins in order to ascertain the minimum quantity of lime necessary to assure an excess beyond that required to react with both the casein and the silicate.

The eleven caseins used included some commercial samples but were mostly those furnished by Mr. Dahlberg; they were fairly representative of the various types ordinarily encountered.

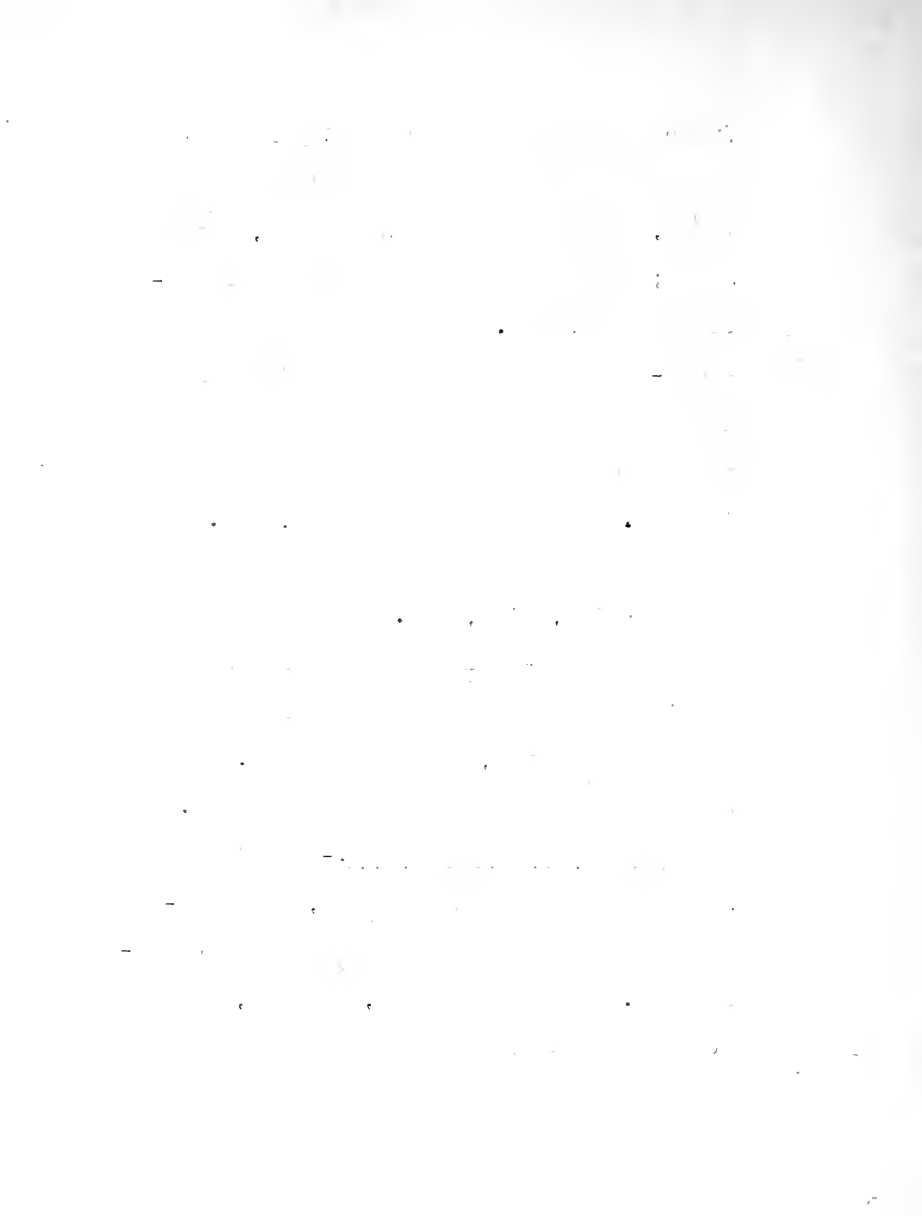
With regard to the preparation of the glues, it was anticipated that, since higher lime content was now to be used, high strength values, comparable with those from the viscous mixtures previously used, could be obtained by resorting to mixtures of lower viscosity. Hence, the amount of soaking water required in each case was



judged as that necessary to impart to the glue a consistency intermediate between a thick, viscous mixture and a thin, watery fluid; this consistency is hereafter described as medium. Where the designations + or - are affixed to the term "medium" it is intended to express a degree more viscous or less viscous respectively than is implied by the term "medium", etc. Record was taken of such glue properties as viscosity, life, etc.

The birch-poplar panel (1/16" stock) specimens and the maple shear blocks were prepared as usual, aged and tested. The corresponding data appears in Table IV.

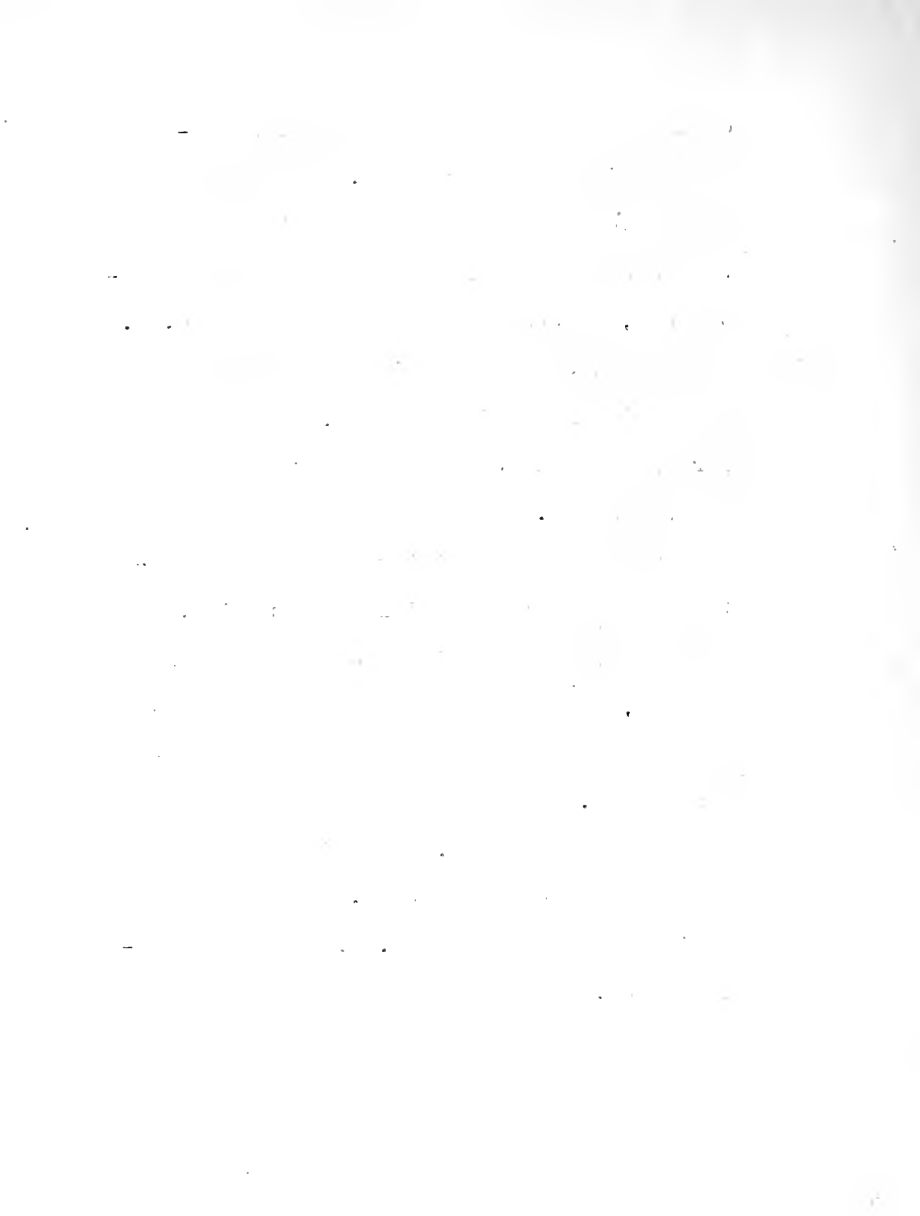
Results and Discussion.--Within the range of caseins investigated, modifications I and II pass the boiling test equally well. Modification II, however, appears more satisfactory in that practically all



of the glues prepared pass the cold water soaking test perfectly. The strength values compare satisfactorily with the high values observed for the relatively more cumbersome, viscous mixtures of formula No. 3. As was anticipated the increased lime caused a material reduction in life, the latter varying from 4 to 23 hours depending upon the viscosity.

Casein VIIB exhibited abnormal behavior due apparently to inferior quality. It had a very offensive odor when prepared as glue, and its long life was apparently due to failure to gel because of hydrolytic action.

Modification No. II having different properties from formula No. 3 is hereafter designated as formula No. 4. It is presented below.



100 parts casein)	Soak	
- parts water)	1/2 hour)	
+)	
15 parts powdered))	
hydrated lime))	
90 parts water))	Mix
+)	
70 parts silicate)	

Proving of Formula No. 4

The preceeding limited application of formula No. 4, while it indicated that satisfactory results could be obtained in general, was not considered conclusive. Through the efforts of Mr. Dahlberg, a very large number of caseins had been prepared which varied both in their methods of preparation and in the factors affecting manufacture. It was proposed to apply the formula to all of the caseins available and to have the caseins submitted to routine analysis. It was hoped that from this great accumulation of data relations would appear between the glue-making qualities of caseins, their methods of manufacture, their chemical analy-



ses, and their physical properties.

A new test designed to determine shear strength of plywood had now been perfected, as a supplement to the usual method of tests, which it becomes necessary to describe at this point.

Tension Shear Test.--It is readily obvious that a shear test of plywood differs from the usual compression-shear tests on maple specimens in that the grain of contiguous layers lie at right angles to each other, whereas in the case of maple shear blocks parallel grain is encountered. Accordingly much lower strength values are to be expected from plywood shear tests.

The specimens for this test are cut (from the veneer panel) according to the form and dimensions shown in Fig. 6. These are then inserted in the jaws (Fig. 7) of the Riehle testing machine shown in



Fig. 8. A schematic diagram illustrating the operation of the latter is presented in Fig. 9.

In using the machine the horizontal beam carrying the load B and the counterweight W is levelled by regulating the amount of shot in the hopper B. If shot is removed from B the beam is thrown out of balance by the action of the counterweight W which causes depression on the right about the knife edge at A. The beam can now be brought back into the horizontal by applying a downward force at C, (through the aid of a handwheel) which is transmitted back through the specimen and the system of lever and links DEF to the beam, causing rotation about A in the opposite direction.

In actual test the beam is brought into the horizontal, the specimen inserted,

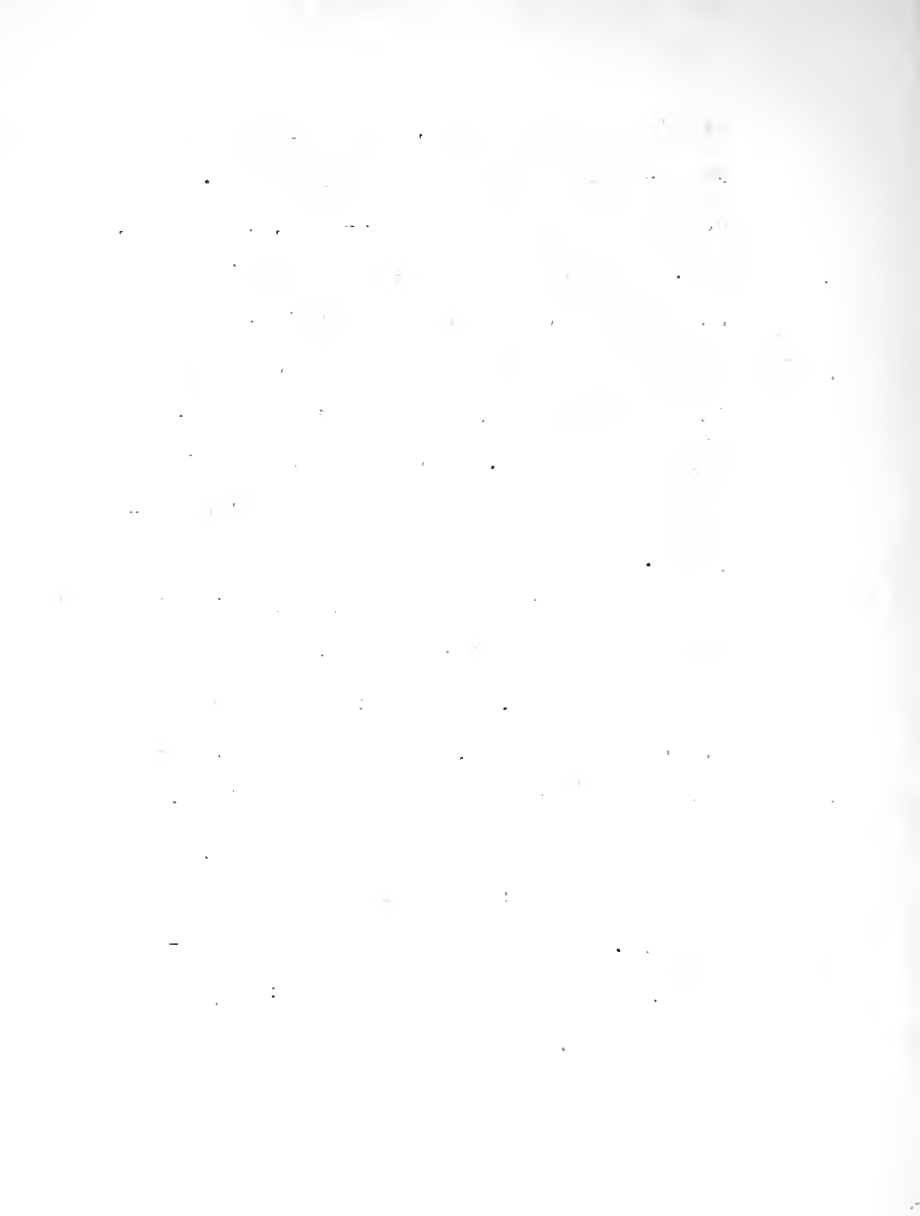
and a continuous stream of shot allowed to discharge from B into the receptacle A. The handwheel which delivers the force at C is now put into rotation at a rate sufficient to take up the yield in the specimen and thus maintain the beam horizontal. In this manner all of the load due to the loss of shot from B is thrown on the specimen. At rupture, the corresponding load is read on the calibrated face of the scale at X which gives the strength in shear in pounds per square inch directly.

From the direction of the forces applied in this device to shear the specimen the test is called tension-shear test.

Method of Procedure.--The procedure followed in the application of formula No. 4 to the various caseins was identical with that described in the preliminary an-

alysis of the formula, veneer panel and shear-block specimens being prepared. Record was taken of the glue-life, viscosity, etc. The boiling and soaking specimens were cut into the form of tension-shear specimens in order that these would be in proper form for shear test after removal from water. Specimens for tension shear test in the dry state were also prepared.

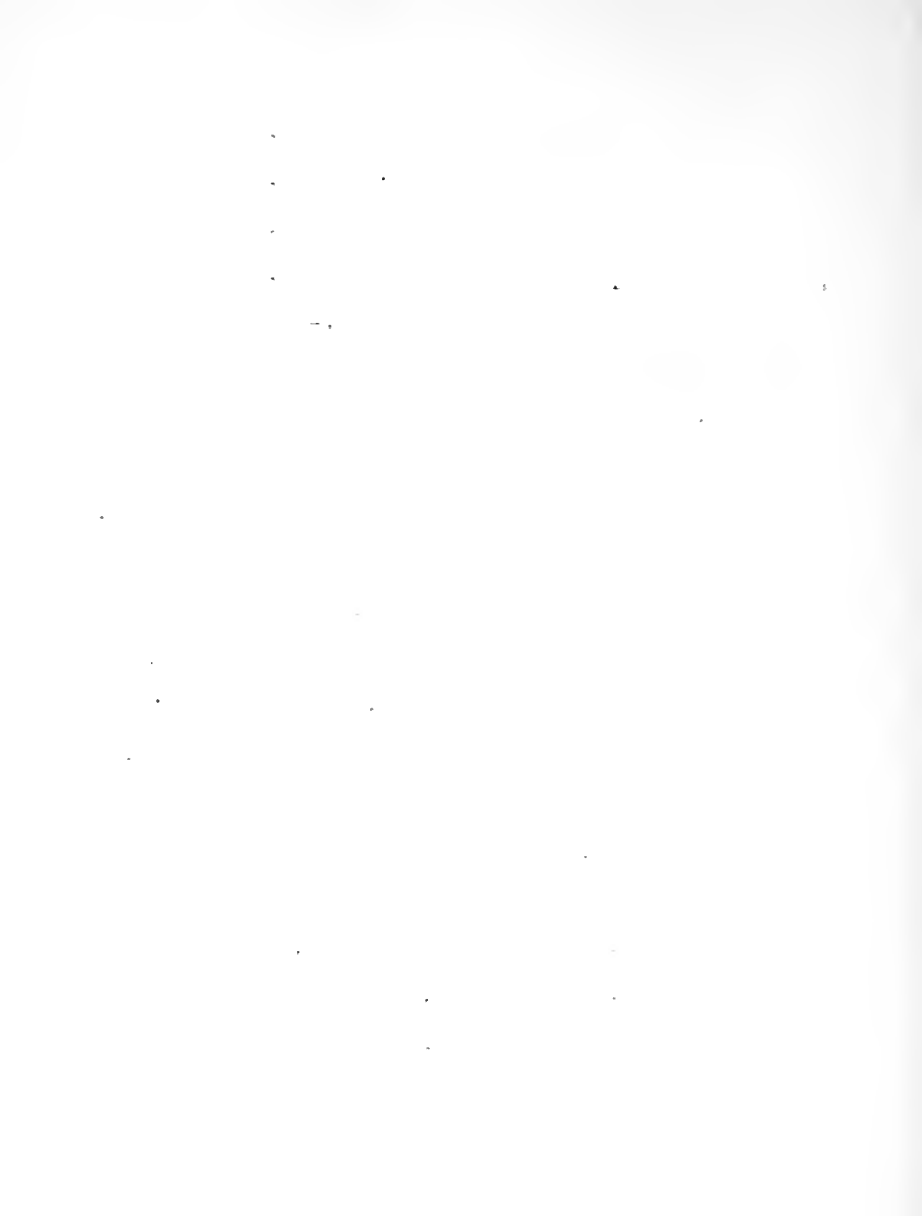
The caseins used in the investigation numbered eighty six; seventy-three were furnished by Mr. Dahlberg; twelve were commercial samples, and one sample (rennet casein) was prepared by the writer. The lime employed was a high grade calcium lime analyzing practically 99% Ca(OH)_2 . The silicate of soda used exhibited the following analysis:



Specific Gravity	1.38
Density (Beaume scale)	40.31°
Na ₂ O	9.38%
SiO ₂	30.50%

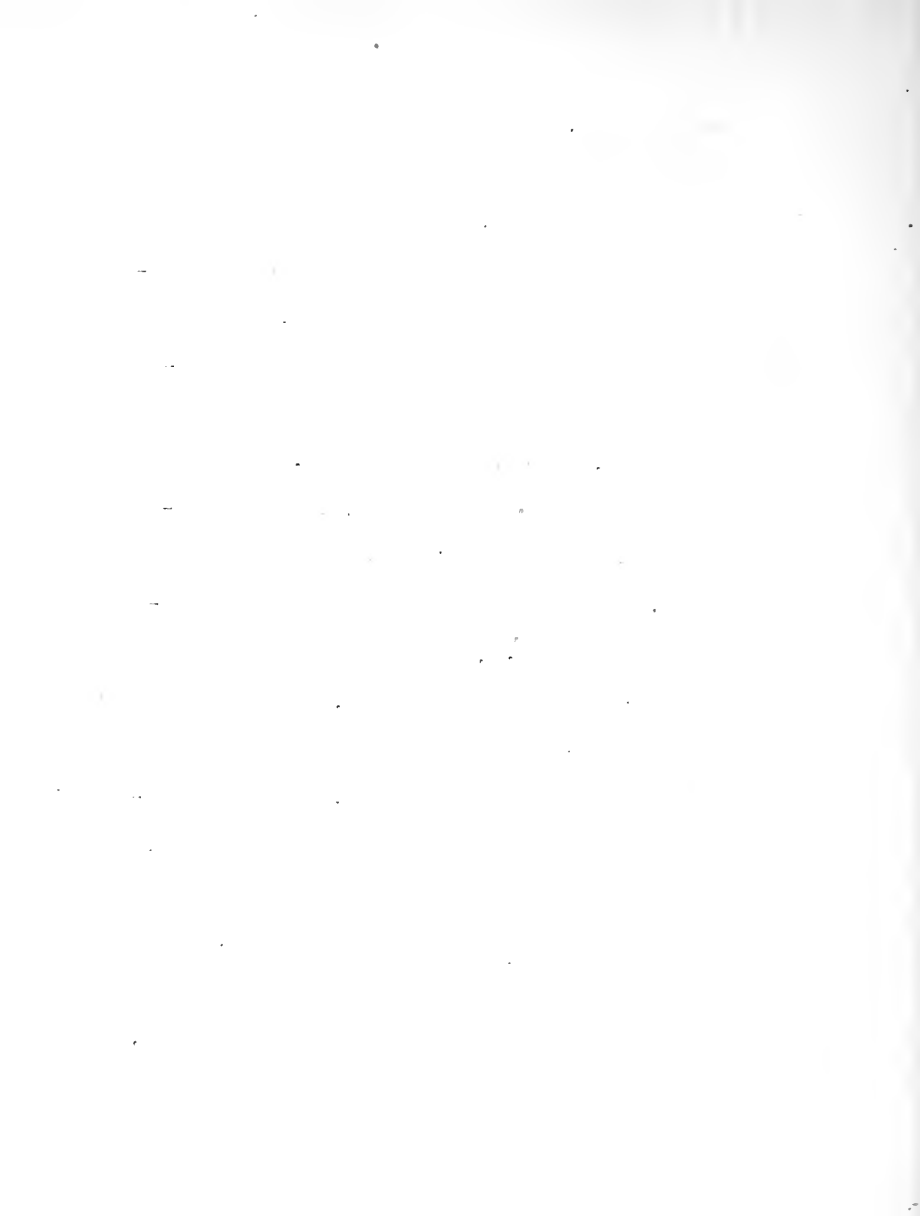
Results and Discussion.--The data derived from the investigation are arranged in Table V.

Study of this table shows that all of the caseins pass the boiling test perfectly. While the results of the soaking test are not quite so satisfactory, it appears that all caseins of reasonable purity will pass this test satisfactorily. It is consistently recorded that caseins of inferior quality, such as develop offensive odors when made into glue, will complete the test with a grade lower than B and hence are not satisfactory. These caseins, then, should be avoided. In general, with regard to water-resistance qualities, it may be said that



formula No. 4 will produce satisfactory glues with most caseins of a reasonable degree of purity. Indication is that special cases may be found in which somewhat more lime may be required. Such special instances will have to be remedied according to the circumstances of the case, whenever they occur.

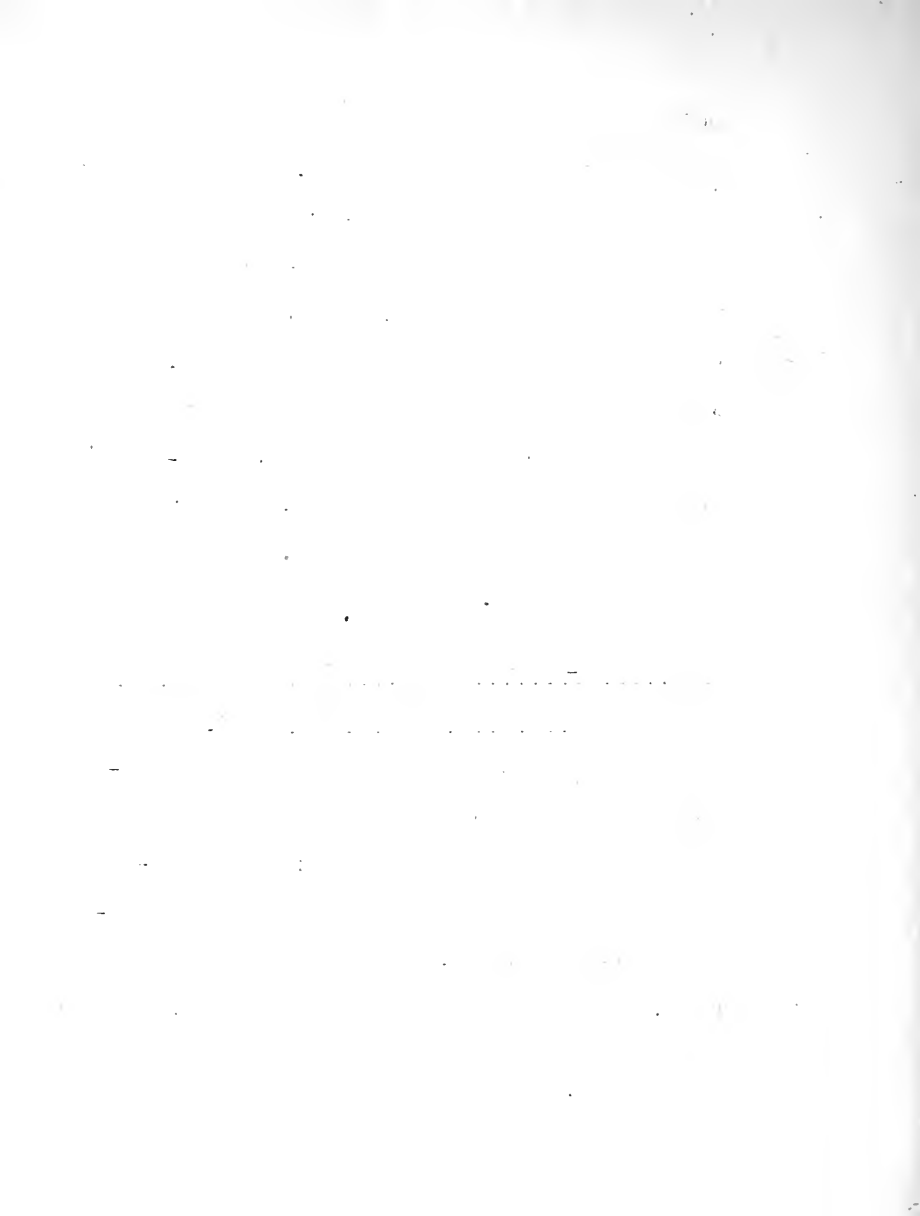
The strength of the glue seems independent of the nature of the casein used. Values in compression-shear average $2400\# / \text{in.}^2$, taking the nature of the failure into consideration. The strength in tension-shear averages about $300\# / \text{in.}^2$ with the type of jaws used. Since eccentric loading is not entirely eliminated, this value would undoubtedly be somewhat higher with properly designed jaws. The water saturated specimens are seen to undergo a material reduction in strength,



boiled specimens being more seriously affected than the soaked ones. It is regretted that these water-saturated specimens were not tested immediately upon removal from water, in consequence of which the values given are too high. It is felt that a conservative estimate of the average strength of the wet plywood tested would be $150 \frac{\text{lb}}{\text{in.}^2}$ for soaked specimens and $100 \frac{\text{lb}}{\text{in.}^2}$ for boiled specimens.

Section V - Factors Responsible for Diverse Character of Caseins

In the preceeding text it has been repeatedly pointed out that technical caseins vary widely in their behavior; the annoyances arising from this situation have likewise been indicated. With these facts in mind, a comprehensive study of the data of Table V reveals much information bearing



directly upon this immediate circumstance. An analysis will readily confirm the following observations.

Influence of Manufacturing Conditions

On Chemical and Physical Nature.--

The chemical nature and physical properties of caseins from skim milk depend chiefly upon the method of precipitation and the subsequent treatment. Commercial caseins containing the smallest amounts of impurities (ash) are produced by the so-called "grain-curd" method. This is a relatively new process and has not yet been widely adopted. It is capable of producing caseins as low in ash as one per cent, although the average is probably nearer 1.8 per cent. Mineral acid caseins are relatively higher in ash averaging probably in the vicinity of 4 per cent. Natural-sour caseins approach the low ash content of grain-curd

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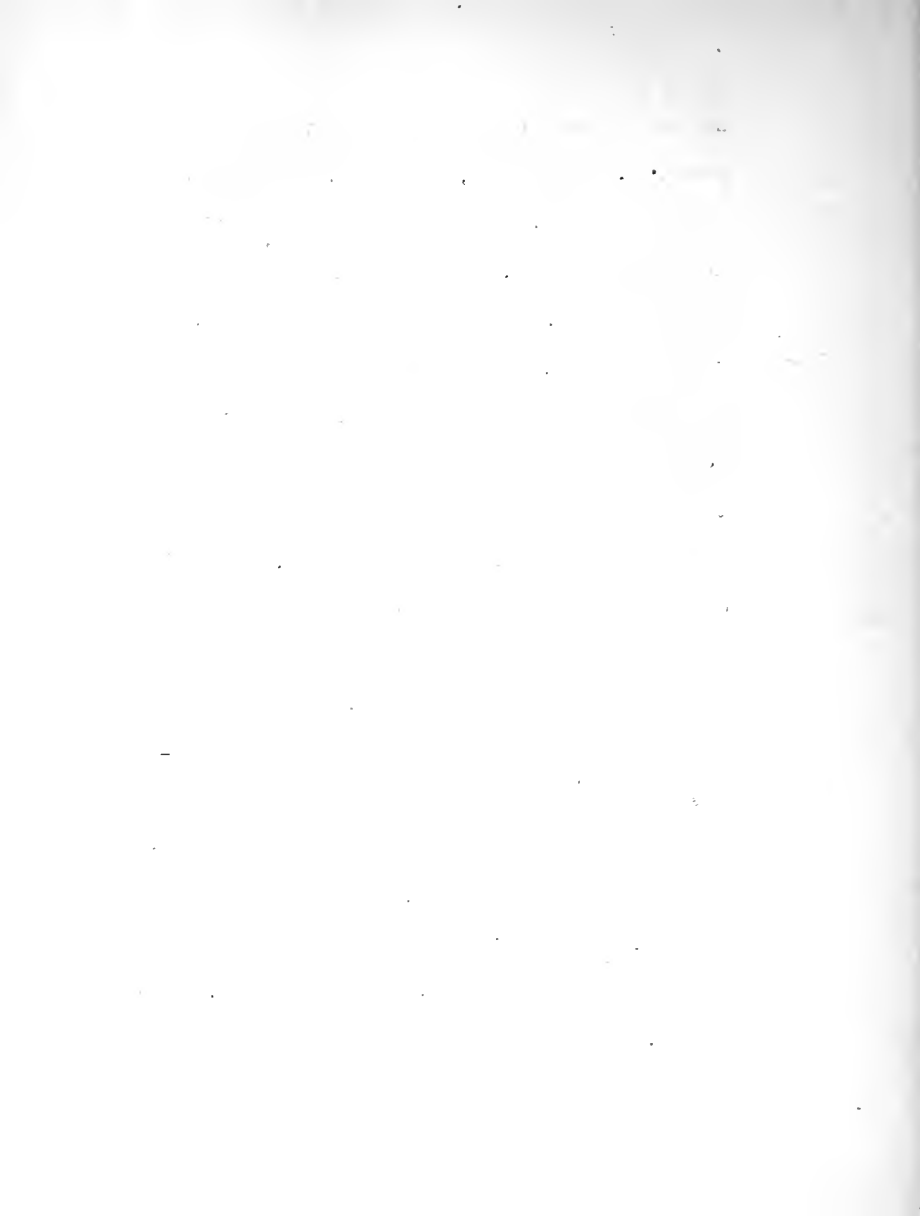
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casein more closely with an average of about 2.5 per cent, as ordinarily prepared by the vat method. This relatively low ash content, compared with mineral acid caseins, is ascribable to the fact that in the natural sour process the development of acid is gradual and thus occurs uniformly throughout the charge; this local presence of acid combined with the prolonged period of contact, typical of the method, serves to dissolve from the casein considerable of the mono-calcium phosphate (CaHPO_4). The mineral acid caseins on the contrary are in contact with acid for a very limited period of time and on account of the enmass precipitation of the curd, typical of this method, efficient leaching of the impurities is not possible. Rennet casein contains, as a normal constituent the highest



ash content of all of these types of casein. The reason for this is due to the fact that rennet casein contains combined calcium, and, since it is prepared in a medium free from acid any insoluble calcium compounds mechanically held in the curd are not removed.

Effect of Ash and Free Acid

The glue making qualities of caseins are strongly influenced by the effects of the conditions of manufacture as may be seen from a consideration of the following:

Using a fixed quantity of water, glues prepared from caseins low in ash exhibit lower viscosity and longer life than those from caseins high in ash. This is strikingly evidenced (See Table VI) by the relatively greater quantity of water required for mineral acid caseins in order to produce a com-

Table VI - Influence of Ash on Viscosity and Life

Type of Casein	Ash	Free ¹ Acid	Soaking H ₂ O	Ratio Casein	Consistency	Life
	%	ccs				hrs.
Rennet	8.39	-0.7	3.7	medium +		5
Sulphuric	5.10	4.4	2.25	stiff +		3
"	6.03	2.85	2.15	stiff-		4-1/2
"	5.36	1.8	1.85	stiff		6
"	4.29	1.35	1.8	medium		6-1/2
"	4.96	1.06	1.85	stiff		6-1/2
"	5.58	0.4	1.85	medium +		7
"	3.02	2.5	2.1	thin		18
"	2.64	-0.6	1.6	medium-		14
Lactic	2.62	2.8	1.65	medium +		6-1/2
"	2.51	4.0	1.55	medium		10
"	1.81	1.3	1.6	medium-		23

¹Expressed in ccs of N/10 NaOH

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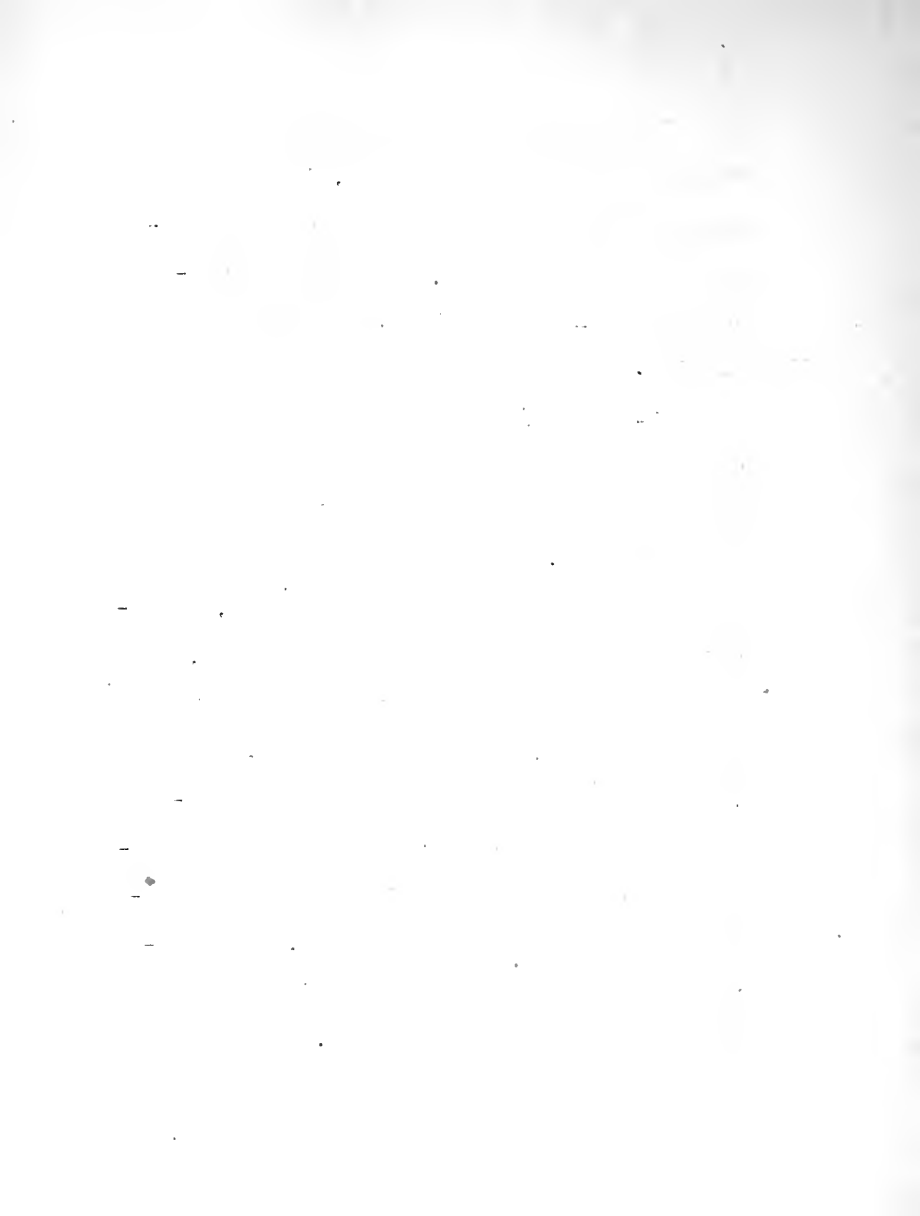
parable viscosity and life, and is even more pronounced in the case of rennet casein which normally contains the highest ash content of any of the types of casein. It is interesting, in this connection, to observe the following figures recently obtained with a grain curd casein, the very low ash content making necessary the use of the smallest quantity of water so far used.

Type of casein	: % Ash	: Soaking : : H_2O : : casein :	: Life : : (hrs.) :	: Consistency
Grain curd	: 1.3	: 1.2	: 12	: medium

It is to be noted that, as the ash content of mineral-acid caseins approaches that of a lactic acid casein, less water is required, and a lower viscosity and a longer life are observed. In the case of lactic caseins the higher the ash, the higher the viscosity for a given water content and the lower the life.

The influence of free acid does not appear to be sharply defined, inasmuch as caseins with a fixed quantity of ash manifest no consistent change either in viscosity or glue life with variation in free acidity.

Further evidence regarding the effect of ash is very strikingly manifested by the behavior of the same casein before and after washing. While both the ash and free acid contents are reduced by washing, apparently from what has already been noted, any change in glue behavior must be attributed to the change in ash content alone. Table VII shows that as the ash content is reduced by washing of the casein the glue viscosity for a fixed quantity of water is reduced and the life is increased. Furthermore because the viscosity is decreased less water is really required.



Graphical Representation of Characteristics.--The general relations just discussed are presented in a very striking manner, if a casein glue-characteristic curve is constructed whose coordinates are ash-content and water-absorption ability corresponding. In the graph given (Fig. 10), four typical points, selected from experience, are plotted - one for each type discussed. The properties of each point have been so selected as to represent the average characteristics observed for the type portrayed. It will be noted that from the region of low ash content to that of high ash content, the points lie practically along a straight line curve, verifying the regular relation-ship which exists.

The data upon which the graph is based are given in Table VIII. The ash content

Table VII. Effect of Washing on Viscosity and Life

Type of Casein:	No. of washings:	Ash: %	Free Acid: ccs	(Ratio):	Soaking: H ₂ O	Consistency:	Life: hrs.
Lactic	0	2.51:	4.0	1.55:	medium	-	10
"	3	1.44:	2.6	1.50:	medium	-	18
"	0	2.46:	3.6	1.45:	medium	+	7-1/2
"	3	1.93:	2.0	1.45:	medium	-	11
"	0	2.20:	3.6	1.65:	medium	-	11
"	3	1.49:	1.7	1.60:	medium	-	16
"	0	2.62:	2.8	1.65:	medium	+	6-1/2
"	3	1.33:	2.6	1.50:	medium	-	13
Sulphuric	1	5.58:	0.4	1.85:	medium	+	7
"	2	3.55:	0.4	1.85:	medium	-	12
"	0	4.27:	1.39	2.0	stiff	-	4-1/2
"	2	5.36:	1.80	1.85:	stiff	-	6
"	0	4.40:	0.1(3)	1.85:	medium	-	6-1/2
"	2	4.15:	-0.1	1.85:	medium	-	9
"	0	3.94:	1.4	1.7	medium	-	9
"	several	2.64:	-0.6	1.6	medium	-	14

(3) The appearance of negative-acidity values is explained by VanSlyke as due to the fact that all of the casein is not base free-i.e., some calcium has come down with the curd in which it is present. Since no correction is made for this impurity all results on free-acidity are necessarily low and in some cases even negative.

has been selected to roughly represent the average contamination peculiar to specific types and the ratio, $\frac{\text{water}}{\text{casein}}$, is such as to produce a medium viscosity in the glue prepared from a casein of the specific ash content given. In the ratio, $\frac{\text{water}}{\text{casein}}$, by the term water is to be understood the soaking water plus that added with the lime, i.e., total water.

Table VIII - Data for Casein Glue-Characteristic Curve.

Type of	: Ash :	(Ratio)
Casein	: % :	$\frac{\text{water}}{\text{casein}}$
	:	:
Grain-curd	: 1.8 :	2.5
	:	:
Natural sour	: 2.5 :	2.45
	:	:
(Ordinary)	:	:
Mineral acid	: 4.0 :	2.8
	:	:
Rennet	: 8.6 :	3.9

The value of such a graph for the purpose of pre-determining the quantity of

water which will be required for a specific casein of known ash content, when made into a glue according to formula No. 4, is verified by checking the curve against the ash content and water absorption ability of the caseins described in any of the accompanying tables. In such a comparison it is well to bear in mind that the water content recorded must be corrected to conform to a medium viscosity, wherever such a viscosity did not actually exist, inasmuch as the graph was constructed for glue preparations of medium viscosities.

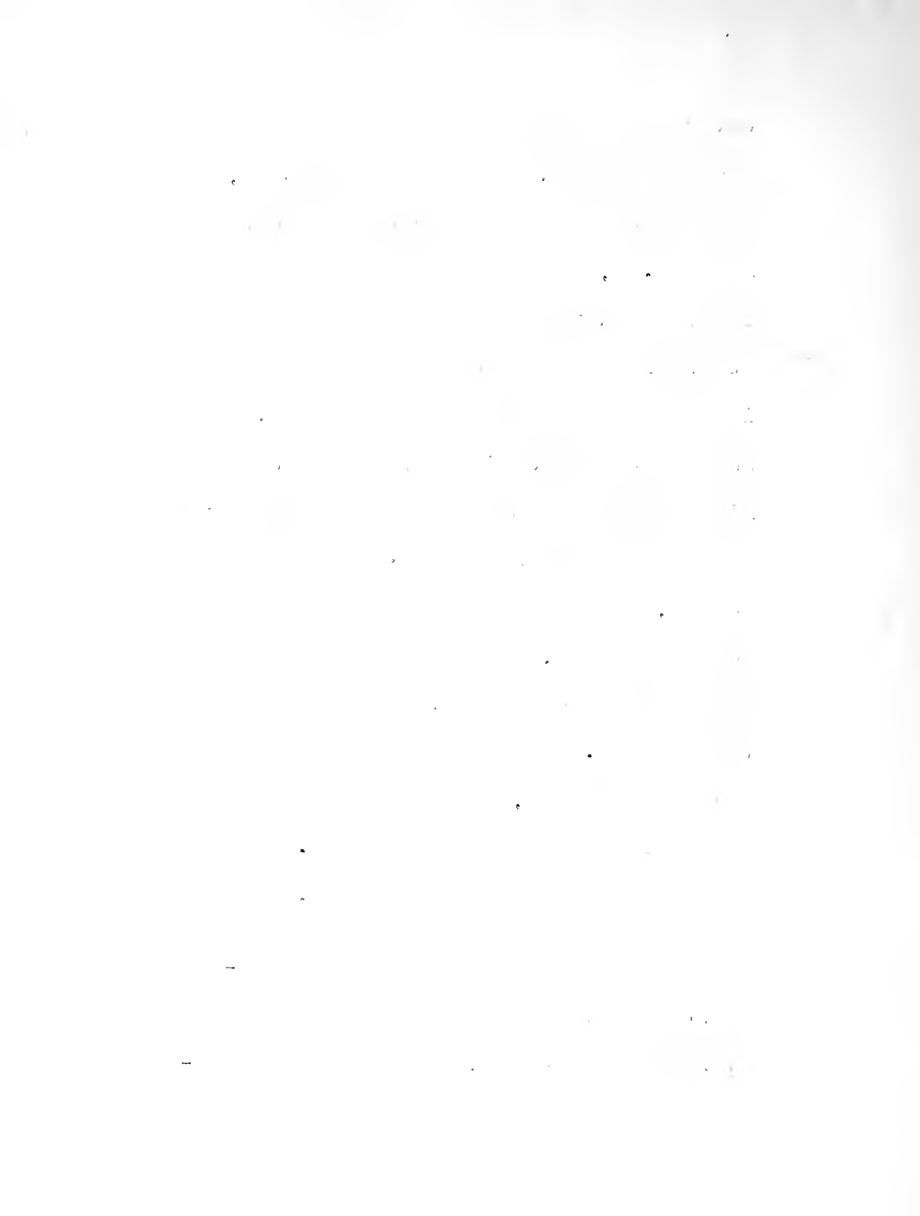
For example, from Table VI

Per cent Ash	6.03
--------------	------

<u>Water</u>	5.05
Casein	

Consistency	Stiff -
-------------	---------

These observations were not made on a glue of medium viscosity, hence the water re-



quirement must be changed to be comparable with the curve. The corrections to be added in any case, to the ratio, $\frac{\text{water}}{\text{casein}}$, whenever the viscosity recorded is not medium, are given below for the corresponding viscosities shown.

thin	- 0.4 parts
medium -	- 0.2 "
medium +	+ 0.2 "
stiff	+ 0.3 "

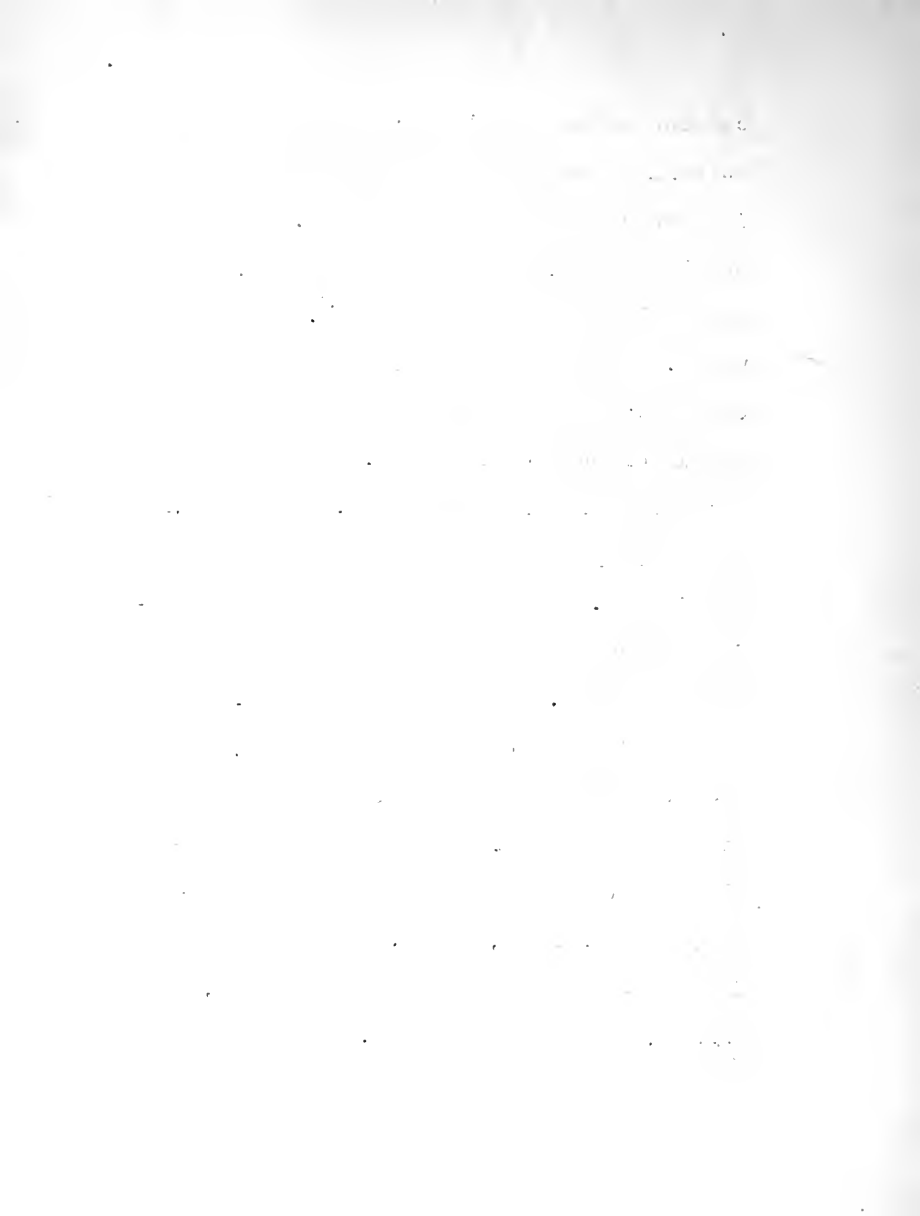
Making the proper correction, the ratio, $\frac{\text{water}}{\text{casein}}$, in the above extract from Table VI becomes 3.25. On reference to the graph, it is seen that this figure checks the graph.

It is to be expected that slight discrepancies between observed requirements and those prescribed by the graph will be encountered since the observation of consistency is but approximate at best.

If the curve be continued by extending the straight line in the dotted portion shown,

caseins which do not fall within the range actually investigated may be included in its scope by this extrapolation. It may now be predicted that a pure casein, free from ash would require about 1.85 parts of water. The nearest approach to such a casein is one recently made available from the laboratory of VanSlyke. Its ash content determined in platinum was 0.38 per cent. The graph prescribes that such a casein requires 1.95 parts water per part of casein to form a glue of medium viscosity. On actual test 2.1 parts were required.

It is now possible by deriving the equation of the straight line graph to make available a mathematical relation between the ash content of a casein and its corresponding $\frac{\text{water}}{\text{casein}}$, ratio. For simplicity in the following discussion the ratio, $\frac{\text{water}}{\text{casein}}$, is designated by W. Writing the

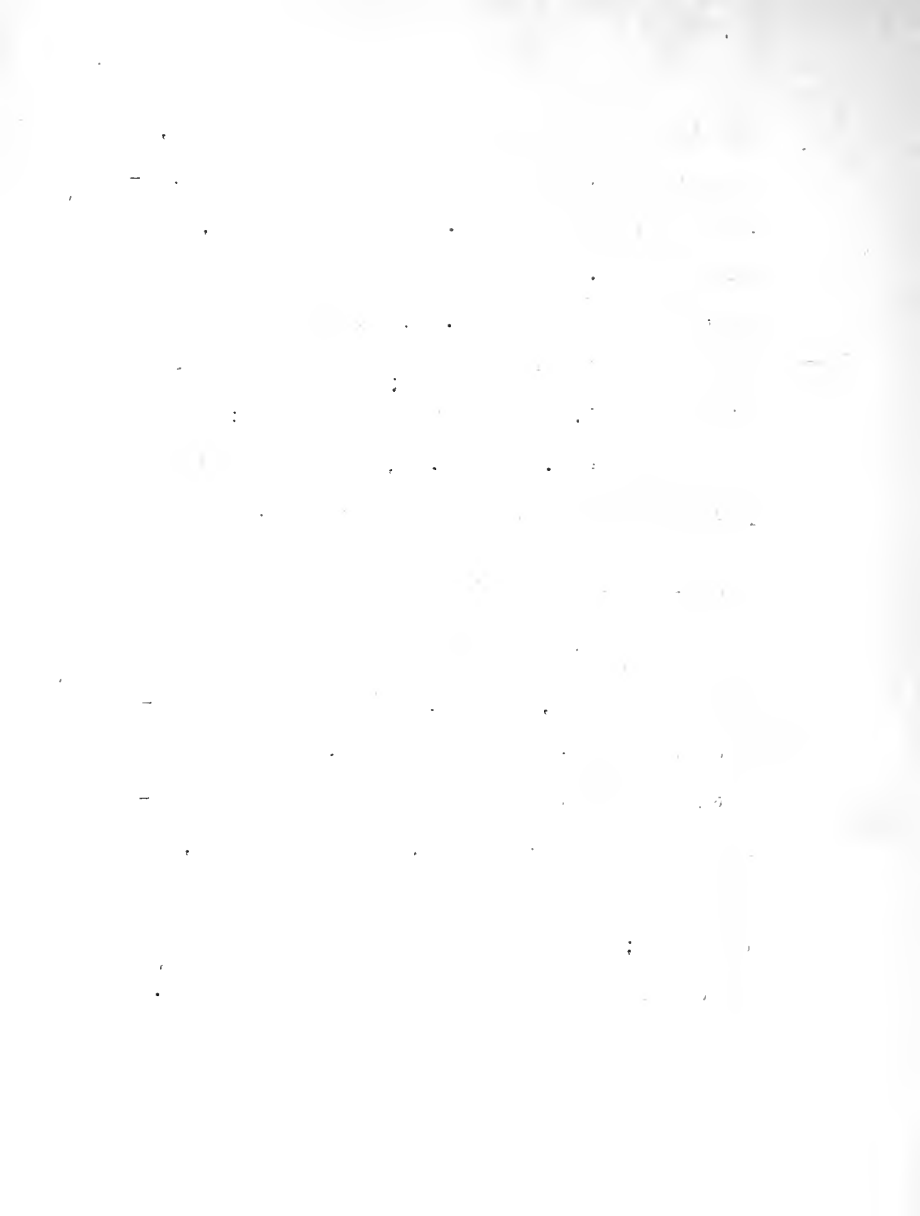


equation of a straight line as $y = mx + c$, the constants may be evaluated from the following considerations. From the graph, a casein of 0.0 per cent ash content has a value of W equal to 1.85, and the slope of the line being observed by simple inspection to be 0.24 the equation becomes:

$Y = W = 0.24x + 1.85$, where x equals per cent ash content of the casein.

BIBLIOGRAPHY ON CASEIN AND CASEIN GLUES

No special treatises are available in the literature, as yet, on the special subject of water-resistant glues. By selecting from the following bibliography much information regarding casein, its properties, preparation and technical utilization can be obtained; occasionally references to the use of casein in glue preparations also occur.

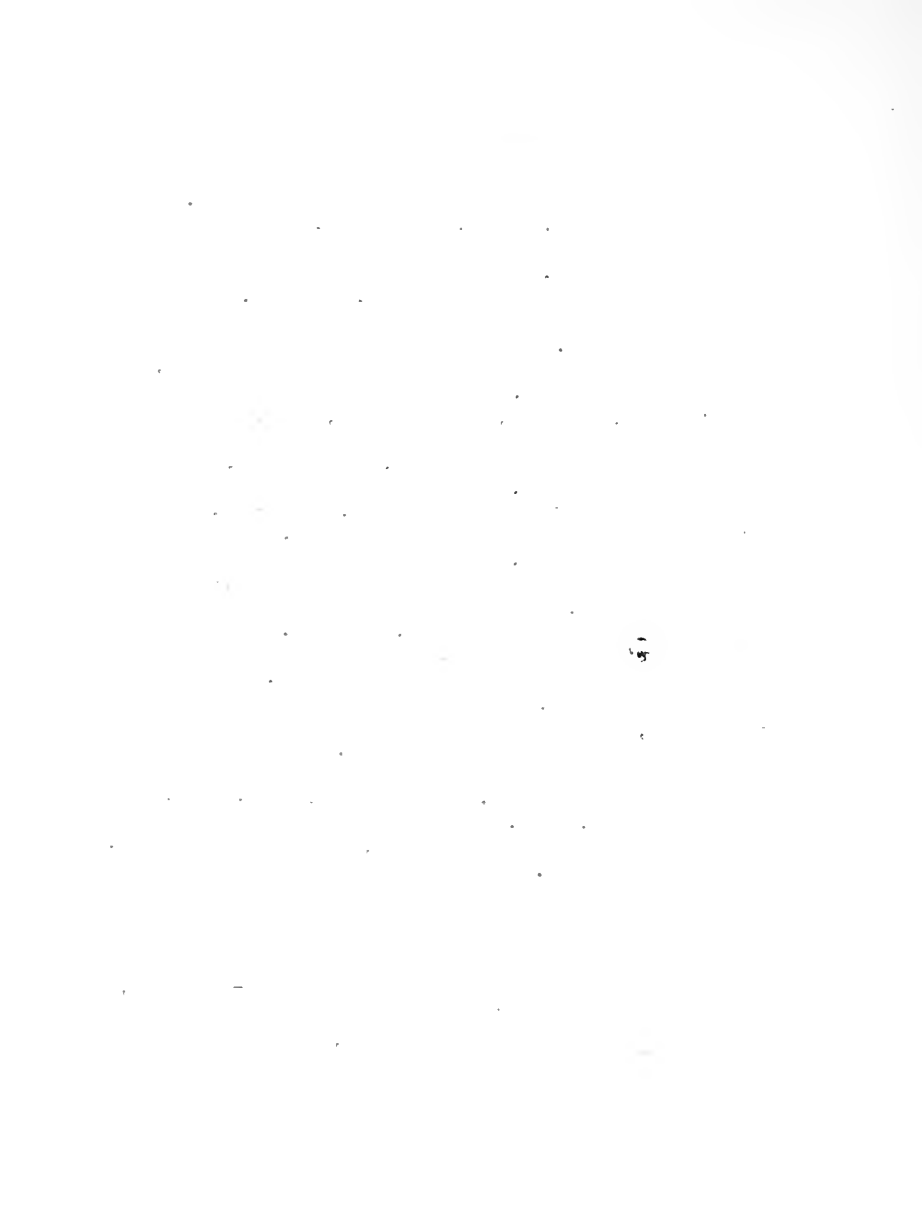


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- "General Characteristics of Proteins."
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- "Chemistry of the Proteids." Mann.
- "Chemical Constitution of the Proteids."
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Mandel.
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- 1 "Industrial Chemistry." Rogers & Aubert.
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- 1 "Casein, its Preparation and Technical
Utilization." Scherer.
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- 1 Contains information on casein glues.



- "Casein and its Technical Applications." - Marotta, Annali di Chimica Applicata, v. 6, p.165.
- "Casein, its Utilization in the Paper Industry." World's Paper Trade Review, v.46, pp.281,657.
- "Casein." Reuter, Papier - Zietung, v.32, pp. 3286, 3374.
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	848,746)	
	183,024	Ross
	21,744	Gardner, 1896
	609,200	Hall, 1896 (Reissue
		11,811,1900)

A large number of articles have been published on the chemical properties of pure casein. They can be located through

1. The first part of the document discusses the importance of maintaining accurate records of all transactions and activities. It emphasizes that proper record-keeping is essential for transparency and accountability, particularly in financial matters. The text suggests that organizations should implement robust systems to track every detail, from procurement to sales, to ensure that all data is reliable and accessible.

2. In the second section, the focus shifts to the role of technology in modern business operations. It highlights how digital tools and software can streamline processes, reduce errors, and improve overall efficiency. The author argues that embracing technology is not just a luxury but a necessity for staying competitive in today's fast-paced market. Examples of various software solutions and their benefits are provided to illustrate this point.

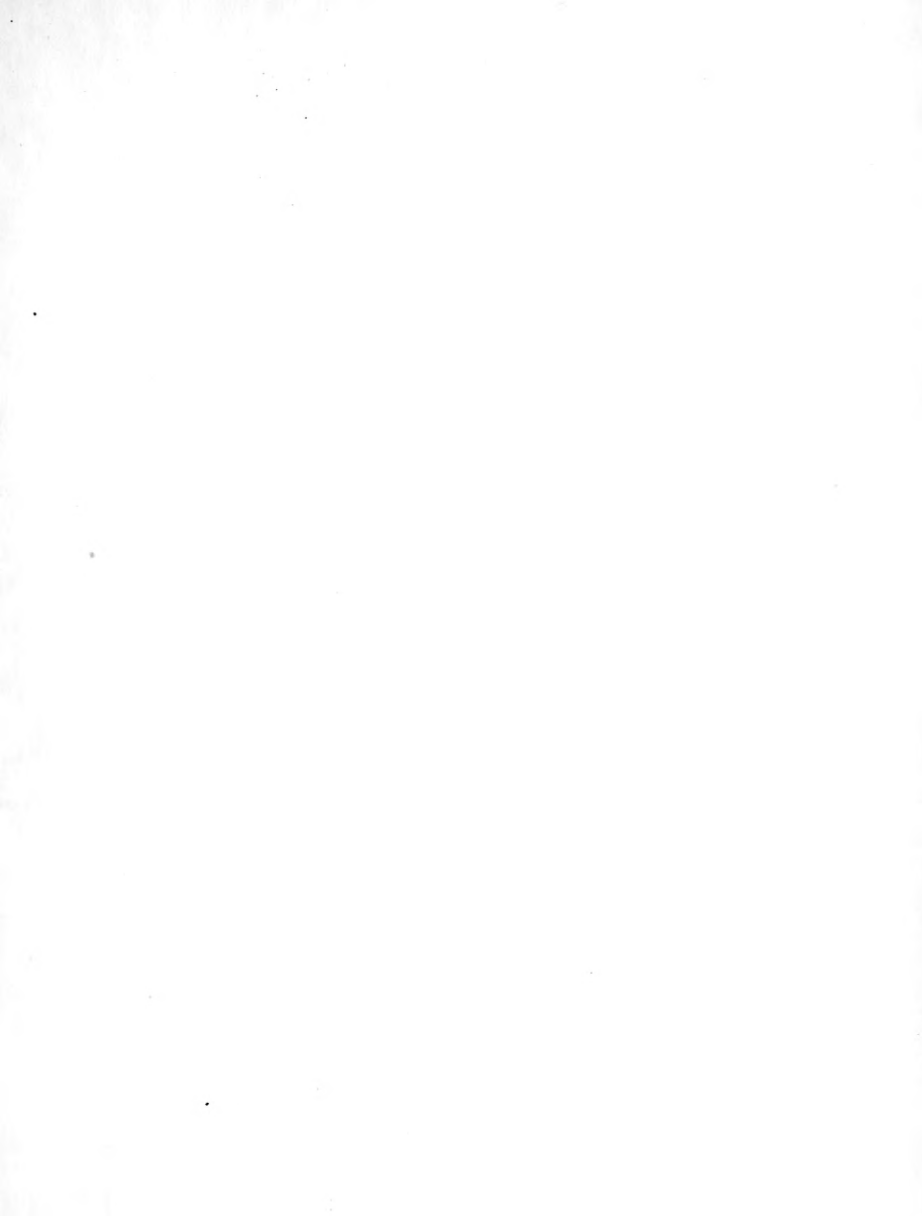
3. The third part of the document addresses the challenges of managing a diverse workforce. It discusses the importance of effective communication and collaboration across different departments and cultures. The text offers practical advice on how to foster a positive work environment, resolve conflicts, and motivate employees. It also touches upon the need for continuous training and development to keep the workforce up-to-date with the latest industry trends.

4. The fourth section explores the impact of external factors on business performance. It examines how economic fluctuations, regulatory changes, and market trends can influence an organization's success. The author provides strategies for monitoring these external factors and adapting the business strategy accordingly. It stresses the importance of being proactive and flexible in the face of uncertainty.

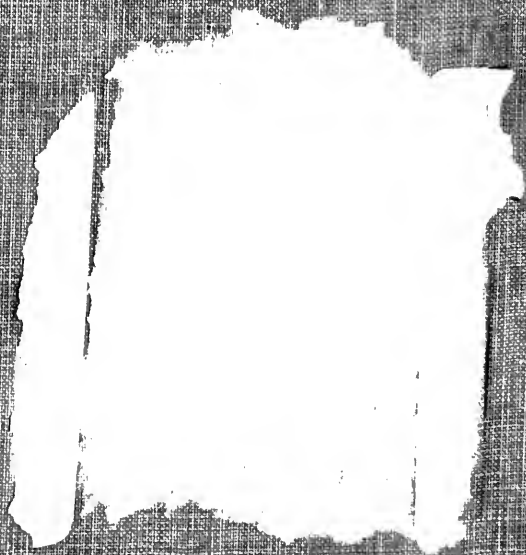
5. Finally, the document concludes with a summary of the key points discussed. It reiterates the importance of accurate record-keeping, the adoption of technology, effective workforce management, and the ability to adapt to external changes. The author encourages organizations to take a holistic approach to business management, ensuring that all aspects of the organization are aligned and working towards common goals.

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Journal of Biological Chemistry
Journal of Physical Chemistry
Journal of the American Chemical
Society
Technical Bulletins of the New York
Agricultural Experiment Station.









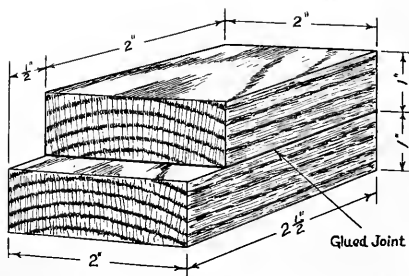
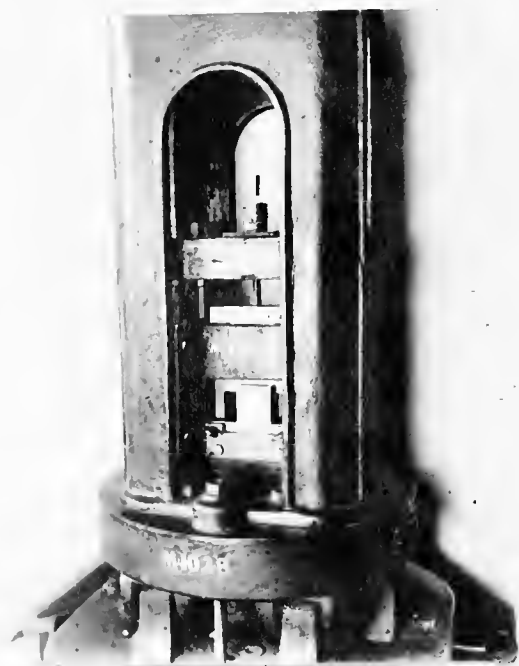
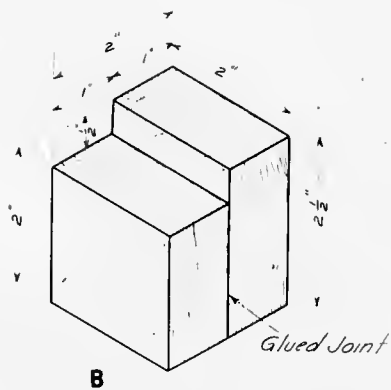


Fig. 3 —Standard Test Specimen for Testing Adhesiveness.

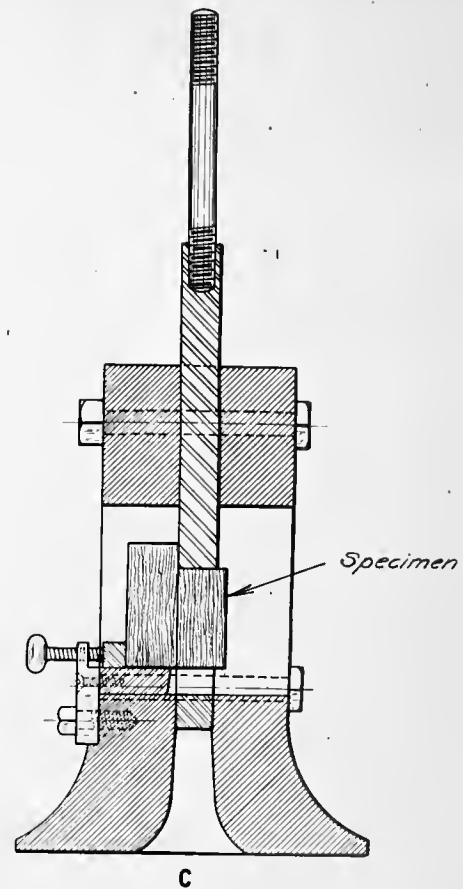


A

6239 M.



B



C

Fig. 4

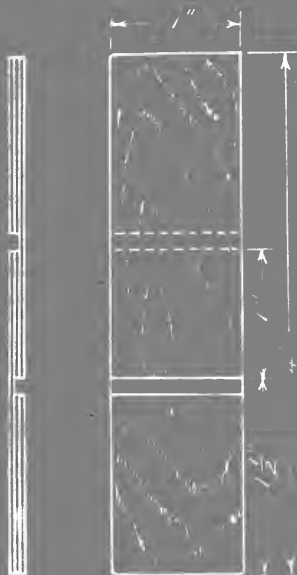


FIG. 6

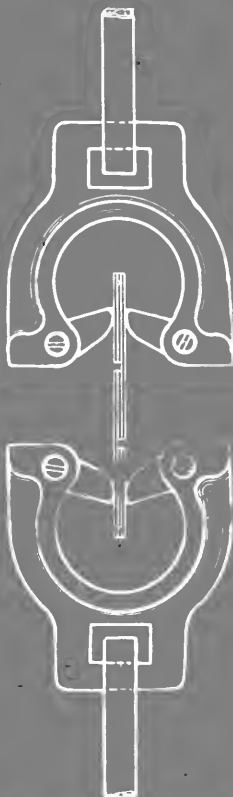
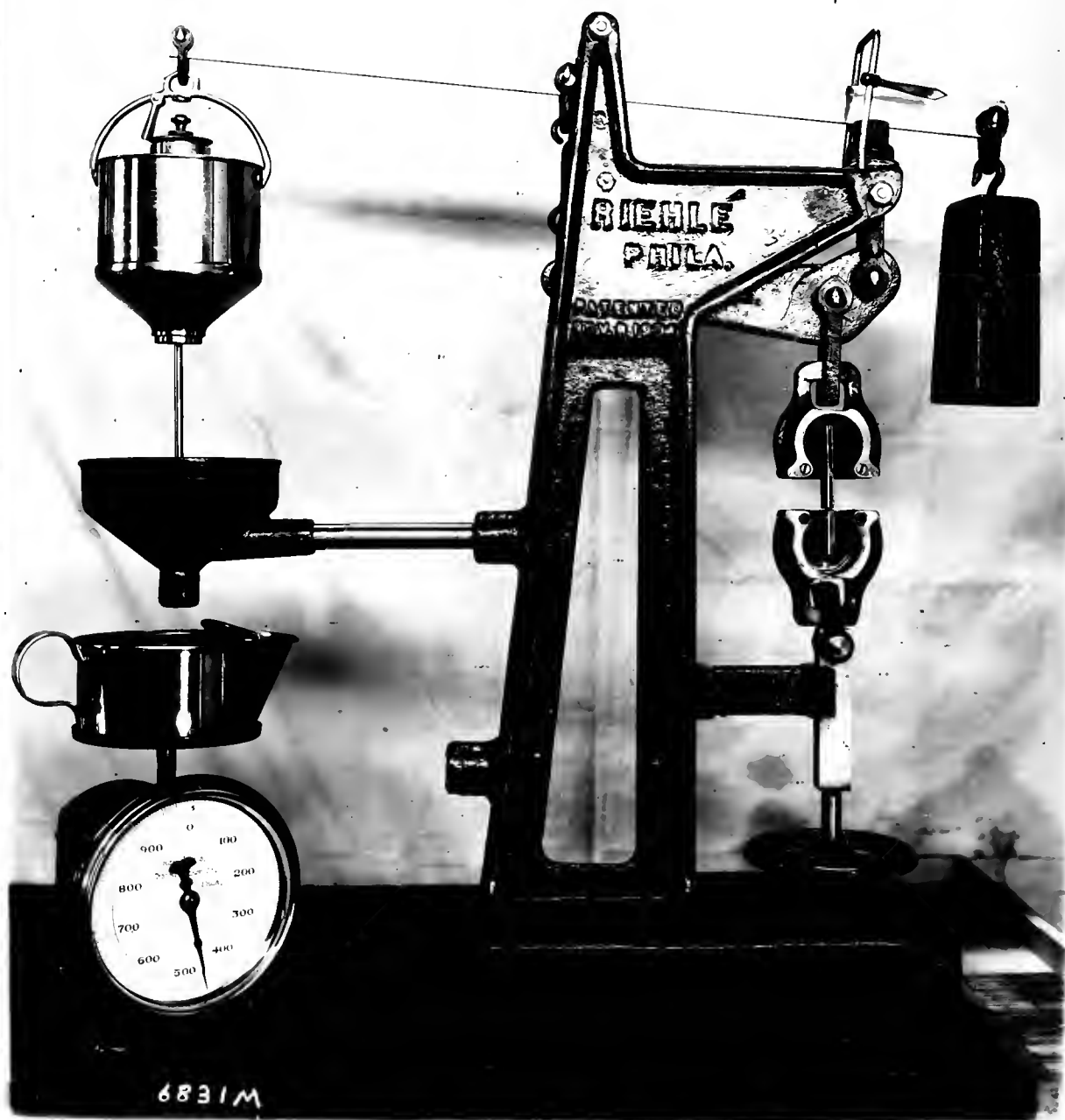
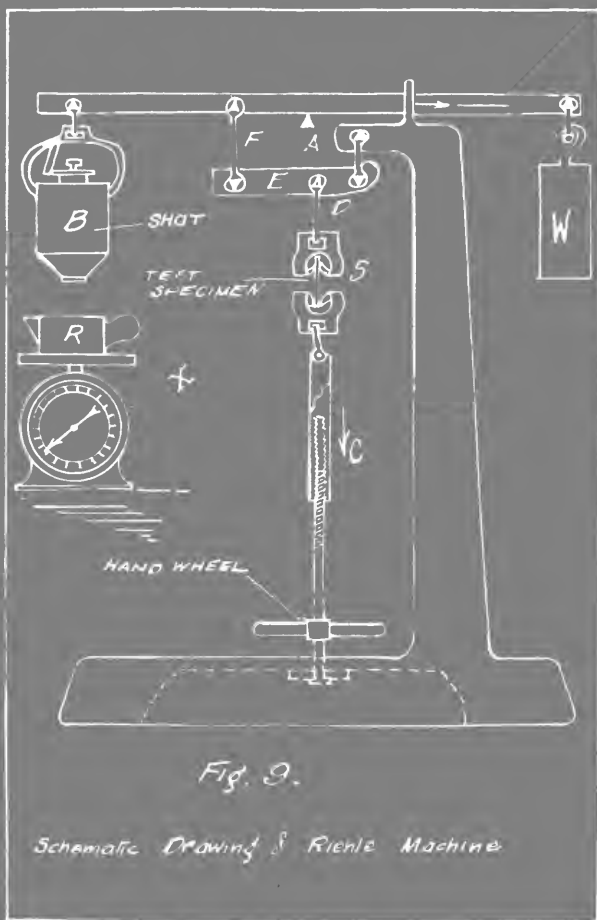


FIG. 7

PLYWOOD SPECIMEN
and
METHOD OF TESTING

U.S. DEPARTMENT
OF
AGRICULTURE
FOREST SERVICE
WASHINGTON, D.C.
JULY 1918





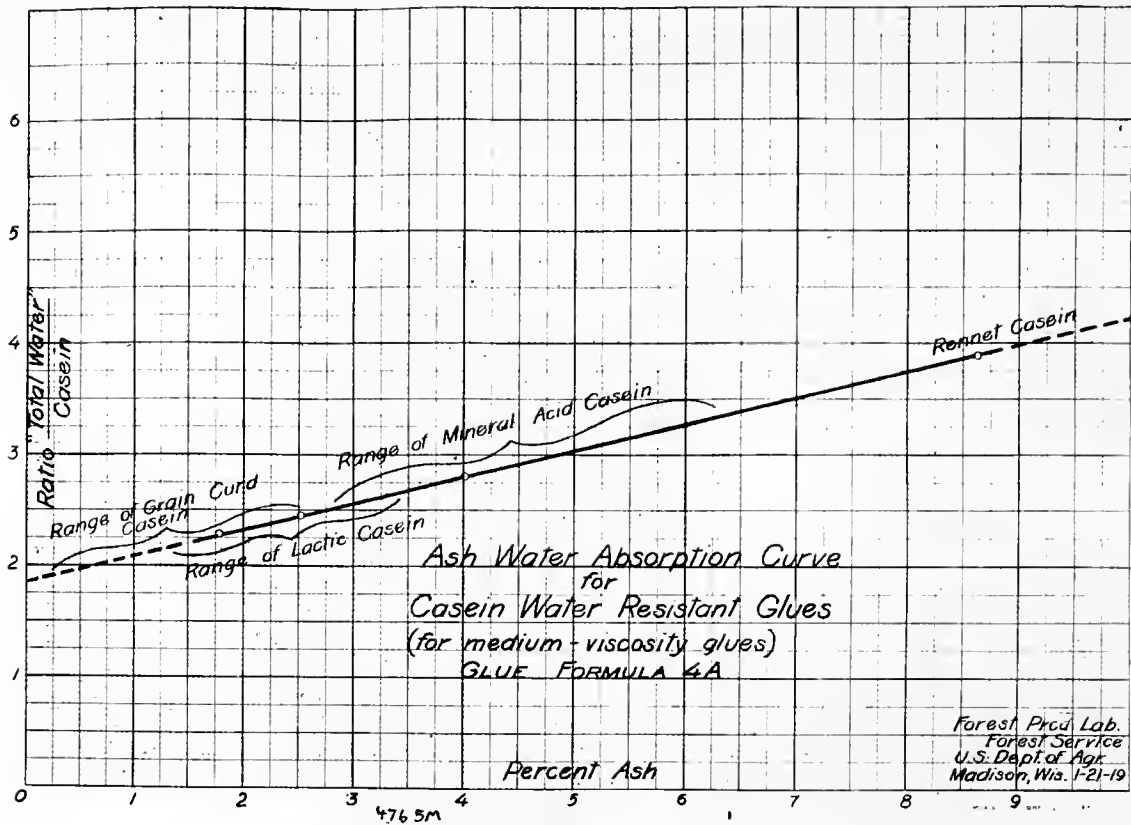


Fig. 10

Forest Prod. Lab.
Forest Service
U.S. Dept. of Agr.
Madison, Wis. 1-21-19

Table III - Results of tests with formula No. 3.

Sample	Manufacture	Ratio (by weight) Soaking water to Casein	Corresponding Consistency	Life in Hours	Boiling Test	Soaking Test	Strength in Shear			Nature of Failure	
							Maximum	Minimum	Mean	Wood	Maximum : Minimum
							Lbs. per sq. in.	Lbs. per sq. in.	Lbs. per sq. in.		
96C (a)	Ejector Method	1.55	Stiff	20	A	D	3880	2790	3000	85	75
95A	"	1.55	"	30+	A	D	2860	1930	2599	70	10
95B	"	1.55	"	35+	A	D	1840	2380	3701	75	80
33B	"	1.60	Medium +	55+	A	D	---	---	---	---	---
XV-B	(b) Lactic (c)	1.35	Stiff	50+	A	D	2625	2095	2396	0.0	10
XVI-B	(b) Lactic (c)	1.35	"	50+	A	D	2900	2250	2634	0.0	0.0
59-C	Ejector Method (Knowles)	2.60	Watery	58+	A	D	2120	1695	1955	0.0	0.0
59-C 1	"	2.00	Medium	63+	A	D	3020	2450	2687	10	10
59-C 2	"	1.70	"	55+	A	D	3110	2345	2777	90	50
59-C 3	"	2.00	"	60+	B	D	2345	1977	2185	0.0	0.0
61-D	"	1.70	"	61+	A	D	2940	2195	2624	100	10
61-D 2	"	1.75	Thick	32+	A	D	3295	2650	2950	10	100
34-B	"	1.75	"	---	A	D	---	---	---	---	---
B 2	"	1.75	Medium	70	D	D	---	---	---	---	---
60-C	"	1.60	"	40+	A	D	2800	2600	2716	90	50
C 2	"	1.60	"	43+	A	D	---	---	---	---	---
C 4	"	1.60	Stiff	60	A	D	---	---	---	---	---
22	Ejector Butter-milk	1.75	Medium	88+	D	D	2925	2925	2701	0.0	0.0
61-C	HCl curd cook- ed 158° F.	2.00	Stiff	20	A	D	2610	1975	2249	0.0	0.0
80-C 2	HCl curd cook- ed 146° F.	1.95	Thick +	---	A	D	2920	2650	2770	50	30
34-A	H ₂ SO ₄	1.75	Thick	40+	A	D	2865	2245	2472	0.0	0.0
33-A	"	1.75	"	68+	A	D	---	---	---	---	---
80-A	"	1.75	"	18	A	D	2820	2735	2780	100	30
96-A	"	1.85	"	28+	A	D	2155	1775	1958	70	40
60-A	"	1.75	Very thick	20	A	D	2270	2150	2219	100	60
B 2	"	1.75	"	20	A	D	3080	2385	3016	0.0	50
B 3	"	1.75	"	---	A	D	3055	2320	2677	80	100
61-A	"	2.00	Medium	50+	B	D	2890	2525	2691	50	75
61-A 2	"	1.70	Thick	50+	A	D	2930	2535	2675	60	60
59-A	"	2.60	Very watery	81+	B	D	958	907	918	0.0	0.0
A 2	"	1.75	Thick	20	A	D	3200	3075	3166	10	100
A 2	"	1.75	"	20	A	D	2840	2580	2760	90	100
80-B	H ₂ SO ₄ curd cook- ed 166° F.	1.75	Thick +	20	A	D	3330	2870	3180	60	80
60-A	H ₂ SO ₄ curd cook- ed 175° F.	1.75	"	20	A	D	2460	1845	2170	70	10
96-B	H ₂ SO ₄ curd cook- ed 175° F.	1.85	"	32+	A	D	3120	2420	2780	60	10
59-B	H ₂ SO ₄ curd cook- ed 170° F.	2.60	Watery	80+	A	D	2380	2145	2215	0.0	.40
B 2	"	2.00	Medium	55	A	D	2560	2200	2332	90	.10
B 3	"	2.00	"	56+	A	D	3510	3295	3366	70	50

Note:

The designations + and - which appear in the column headed "Corresponding Consistency" signify a degree slightly greater or less respectively than preceding term.

The designation + which appears in the column headed "Life in Hours" indicates that gelatinization occurred a few hours later than indicated by the figure recorded.

(a) Lactic souring.

(b) Had very sour cheesy odor due to improper drying which had caused slight putrefaction.

(c) Prepared by writer.

Table IV - Results on tests of two modifications of glue No. 3.

Casein		Consistency	Soaking Water: Casein	Life	Boiling: Test	Soaking: Test	No. of Specimens Tested	Strength in Shear					
Mark	Method of Manufacture							Wood		Wood		Average	Wood
								Maximum	Failure	Minimum	Failure	age	Failure
MODIFICATION I								Lbs. per sq. in.	%	Lbs. per sq. in.	%	Lbs. per sq. in.	%
VI11-D:	----	Thin	1.7	27 hrs.	A	A	8	2300	90	1660	60	2008	30
97 B:	Lactic	Medium -	1.45	16 +	A	A	8	3040	75	2550	70	2816	40
59 A:	H ₂ SO ₄	Thick -	1.75	5	A	A	4	2660	60	2550	40	2600	49
33 A:	H ₂ SO ₄	Medium +	1.7	22	A	A	8	2630	10	2320	10	2482	40
96 C:	Lactic	Medium	1.55	20 +	"	"	4	2600	30	1940	20	2356	20
VII-B:	----	Medium	1.9	144 +	"	D	4	2500	20	2190	20	2242	20
60 C:	Lactic	Medium	1.6	29	"	B	8	2280	100	1940	100	2125	91
97 D:	Lactic	Medium	1.6	29	"	A	4	2690	0	2050	60	2505	20
95 B:	Lactic	Medium	1.55	20	"	A	4	2560	85	2175	10	2400	74
95 A:	Lactic	Medium +	1.55	12	"	A	4	2565	20	2450	10	2481	15
97 C:	Lactic	Medium	1.65	18	"	A	4	2500	70	2275	10	2390	41
MODIFICATION II													
VI11-D:	----	Thin +	1.65	12	A	A	4	2690	90	2320	50	2440	57
97 B:	Lactic	Medium -	1.45	11	"	"	4	2920	0	2795	0	2862	0
59 A:	H ₂ SO ₄	Thick +	1.65	4	"	"	8	2775	10	2300	0	2481	0
33 A:	H ₂ SO ₄	Medium +	1.7	10	"	"	8	2680	40	2200	0	2486	39
96 C:	Lactic	Medium -	1.55	10	"	"	4	2560	10	2495	40	2540	15
VII-B:	----	Medium	1.2	192	"	B	4	2680	0	2160	10	2501	42
60 C:	Lactic	Medium -	1.6	23	"	A	8	2725	10	1900	25	2435	60
97 D:	Lactic	Medium	1.6	16	"	A	8	2510	0	2000	10	2285	40
95 B:	Lactic	Medium -	1.5	18	"	A	4	2560	60	2100	85	2400	60
95 A:	Lactic	Medium	1.55	10	"	A	8	2940	10	2040	80	2200	98
97 C:	Lactic	Medium -	1.65	11	"	A	8	2710	30	2075	80	2455	60



